LIST OF THE OFFICERS

OF

The Institution of Petroleum Technologists,

1926-1927.

Past Presidents:

*Sir Boverton Redwood, Bart., D.Sc., F.R.S.E. (1914-1916).
Prof. Sir John Cadman, K.C.M.G., D.Sc., M.Inst.C.E., M.Inst.M.M. (1916-[1917)
Sir Charles Greenway, Bart. (1917-1919).
Sir Frederick W. Black, K.C.B., B.A. (Lond.) (1919-1921).
Prof. John Samuel Strafford Brame, F.I.C., F.C.S. (1921-1923).
Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng. (1923-25).

President:

Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S.

Vice-Presidents:

Alfred C. Adams.
Sir John T. Cargill, Bart.
The Rt. Hon. Viscount Cowdray of Cowdray, G.C.V.O.
Alexander Duckham, F.C.S.
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.
W. R. Ormandy, D.Sc., F.I.C., F.C.S., M.I.A.E.
Robert Redwood, F.C.S.

Members of Council:

Major Sir R. W. Barnett, M.P., M.A.
Ashley Carter, A.M.I.Mech.E.
A. E. Chambers, A.M.Inst.C.E.
E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S.
T. Dewhurst, A.R.C.S., F.G.S.
A. E. Dunstan, D.Sc., F.I.C., F.C.S.
James Kewley, M.A., F.I.C., F.C.S.
E. Lawson Lomax, M.Sc., A.I.C., F.C.S.
Prof. Alfred W. Nash, M.Sc., F.C.S., M.I.Mech.E.
William Sutton, M.I.Min.E.
F. B. Thole, D.Sc., F.I.C., F.C.S.
A. Beeby Thompson, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S.
Prof. W. W. Watts, F.R.S., D.Sc., M.A., Hon.LL.D., F.G.S.

Honorary Treasurer: Sir William Plender, Bart., G.B.E.

Honorary Solicitors: Messrs. Ashurst, Morris & Crisp.

Auditors: Messrs. Price, Waterhouse & Co.

* Deceased.

Bankers:
WESTMINSTER BANK, LIMITED,
21, Lombard Street, London, E.C. 3.

Hon. Editor:
A. E. DUNSTAN, D.Sc., F.I.C., F.C.S.

Assistant Editor:
GEORGE SELL.

Hon. Secretary:
ARTHUR W. EASTLAKE, M.I.Min.E., A.M.I.Mech.E.

Secretary and Librarian:
Commander R. E. STOKES-REES, R.N.

Offices—Aldine House, Bedford Street, Strand, London, W.C. 2.

COMMITTEES:

ELECTION, FINANCE, LIBRARY, PUBLICATION, RESEARCH FUND AND STANDARDIZATION.

Members of the Election Committee.

Sir FREDERICK W. BLACK, K.C.B., B.A. (Lond.).
ASHLEY CARTER, A.M.I.Mech.E.
A. E. CHAMBERS, A.M.Inst.C.E.
T. DEWHURST, A.R.C.S., F.G.S.
ARTHUR W. EASTLAKE, M.I.Min.E., A.M.I.Mech.E. (*ex-officio*).
Sir THOMAS H. HOLLAND, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (*ex-officio*).
JAMES KEWLEY, M.A., F.I.C., F.C.S.
F. B. THOLE, D.Sc., F.I.C., F.C.S.

Members of the Finance Committee.

ALFRED C. ADAMS (*Chairman*).
HERBERT BARRINGER, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng.
ARTHUR W. EASTLAKE, M.I.Min.E., A.M.I.Mech.E. (*ex-officio*).
Sir THOMAS H. HOLLAND, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (*ex-officio*).
ROBERT REDWOOD, F.C.S.
A. BEEBY THOMPSON, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S.

Members of the Library Committee.

Prof. J. S. S. BRAME, F.I.C., F.C.S.
T. DEWHURST, A.R.C.S., F.G.S.
A. E. DUNSTAN, D.Sc., F.I.C., F.C.S.
ARTHUR W. EASTLAKE, M.I.Min.E., A.M.I.Mech.E. (*ex-officio*).
Sir THOMAS H. HOLLAND, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (*ex-officio*).
Prof. ALFRED W. NASH, M.Sc., F.C.S., M.I.Mech.E.
WILLIAM SUTTON, M.I.Min.E.

Members of the Publication Committee.

Prof. J. S. S. Brame, F.I.C., F.C.S.
E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S.
T. Dewhurst, A.R.C.S., F.G.S.
A. E. Dunstan, D.Sc., F.I.C., F.C.S.
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E. (*ex-officio*).
Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (*ex-officio*).
James Kewley, M.A., F.I.C., F.C.S.
E. Lawson Lomax, M.Sc., A.I.C., F.C.S.
W. R. Ormandy, D.Sc., F.I.C., F.C.S., M.I.A.E.
George Sell.

Members of the Research Fund Committee.

Alfred C. Adams.
Prof. J. S. S. Brame, F.I.C., F.C.S.
Alexander Duckham, F.C.S.
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E. (*ex-officio*).
Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (*ex-officio*).
James Kewley, M.A., F.I.C., F.C.S.
Prof. Alfred W. Nash, M.Sc., F.C.S., M.I.Mech.E.
F. B. Thole, D.Sc., F.I.C., F.C.S.
Prof. W. W. Watts, F.R.S., D.Sc., M.A., Hon.LL.D., F.G.S.

Members of the Standardization Committee.

Sir Frederick W. Black, K.C.B., B.A.(Lond.) (*Chairman*).
Prof. J. S. S. Brame, F.I.C., F.C.S.
Alexander Duckham, F.C.S.
A. E. Dunstan, D.Sc., F.I.C., F.C.S.
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E. (*ex-officio*).
Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (*ex-officio*).
James Kewley, M.A., F.I.C., F.C.S.
E. Lawson Lomax, M.Sc., A.I.C., F.C.S.
W. R. Ormandy, D.Sc., F.I.C., F.C.S., M.I.A.E.
Robert Redwood, F.C.S.

Co-opted Members of the Standardization Committee.

Admiralty—Eng. Rear-Admiral W. M. Whayman, C.B.E., R.N.
Government Laboratory—J. J. Fox, O.B.E., D.Sc., F.I.C., F.C.S.
National Physical Laboratory—W. F. Higgins, F.Ph.S., A.R.C.S.
Petroleum Department—J. L. Jeffery, A.R.S.M., M.Inst.M.M.
Air Ministry—G. Rudorf, Ph.D.
War Office—W. L. Baillie, F.I.C.
Arthur A. Ashworth, M.A., A.M.Inst.C.E.
R. G. Batson, A.I.C., M.Inst.C.E., M.I.Mech.E.
S. E. Bowrey, B.Sc.
F. G. Edmed, B.Sc., F.I.C.
E. A. Evans, F.C.S.
F. H. Garner, Ph.D.
J. E. Hackford, B.Sc., F.I.C., F.C.S.
J. S. Jackson, B.Sc., A.I.C.
W. Lee.
A. G. Marshall, M.A.
T. M. McKenzie, A.I.C., F.C.S.
J. McConnell Sanders, F.I.C., F.C.S.
P. E. Spielmann, Ph.D., F.I.C., B.Sc., A.R.C.S.
F. B. Thole, D.Sc., F.I.C., F.C.S.
W. J. Wilson, F.I.C., A.C.G.I.
Walter A. Woodrow, A.I.C., F.C.S.

CONTENTS.

Eighty-ninth General Meeting :— PAGE

The Selection and Properties of Steels used for Oil-Well Boring Equipment, by J. H. S. Dickenson, F.Inst.P., B. Gray, B.A., and F. E. Cherry 1

Discussion : Prof. J. S. S. Brame, Messrs. W. H. Fordham, F. A. Ruddock, A. Beeby Thompson, F. R. Rappoport, Prof. W. H. Merrett, Messrs. T. G. Madgwick and Basil Gray 24

Reply by Mr. J. H. S. Dickenson 29

Ninetieth General Meeting :—

The Vapour Pressures of Fuel Mixtures—Part II., by J. Stanley Lewis, B.Sc.(Wales), A.I.C. 32

Discussion : Mr. E. C. Craven and Dr. A. E. Dunstan 44

Reply by Mr. J. Stanley Lewis 46

Symposium on the Estimation of Unsaturated Hydrocarbons, by Prof. J. S. S. Brame, Dr. A. E. Dunstan, Messrs. E. Lawson Lomax and E. S. Pemberton, Messrs. E. C. Craven and Harold Moore 48

Reply by Prof. J. S. S. Brame 66

Contributed discussion by Dr. F. H. Garner 66

Observations on the Action of Sulphuric Acid on Petrol, by W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven, B.Sc., F.C.S. 68

Examination of Spirit Produced by the Hydrogenation of Coal, by W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven, B.Sc., F.C.S. 77

The Effect of Water on Aniline Points, by W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven, B.Sc., F.C.S. 89

Contribution on Mr. W. H. Cadman's Paper, "The Origin of Hydrogen Sulphide in Persian Natural Gas," by Murray Stuart, D.Sc., Ph.D., F.G.S., F.C.S. .. 92

Reply to discussion on "The Principles of High Vacuum Distillation of Mineral Oils," by L. Steinschneider .. 95

AGE
1
24
29
32
44
46
48
66
66
68
77
89
92
95

CONTENTS.

PAGE

Reviews : " Oil-Field Exploration and Development," Vol. I, by A. Beeby Thompson ; " Report of the Special American Petroleum Institute ' Committee of Eleven ' to the Federal Oil Conservation Board " 97

Current Petroleum Notes 103

Ninety-first General Meeting :—

The Sulphur Compounds of Kimmeridge Shale Oil, by FREDERICK CHALLENGER, D.Sc., Ph.D., F.I.C., JOHN HASLAM, M.Sc., A.I.C., RANDLE JAMES BRAMHALL, B.Sc., and JAMES WALKDEN, M.Sc. 106

Discussion : THE PRESIDENT, Dr. A. E. DUNSTAN, Messrs. J. E. HACKFORD, E. H. CUNNINGHAM CRAIG, E. C. CRAVEN and H. G. SHATWELL 135

Reply by Dr. F. CHALLENGER 137

Ninety-second General Meeting :—

The Search for Oil in Australia, by ARTHUR WADE, D.Sc., A.R.C.S., F.G.S., M.Inst.M.M., F.Am.G.S. .. 145

Discussion : THE PRESIDENT, Dr. J. A. L. HENDERSON, Mr. E. H. CUNNINGHAM CRAIG, Dr. WILLIAM HOPE HENDERSON and Mr. E. PARSONS 164

Reply by Dr. A. WADE 170

Annual Report of the Council, 1925 173

Thirteenth Annual General Meeting 181

Presidential Address, by Sir THOMAS H. HOLLAND, K.C.S.I., K.C.I.E., D.Sc., F.R.S. 187

Eighth Annual Dinner 198

Distillation of Mexican Crude-Oil Emulsions and Simultaneous Preparation of Asphalt Emulsions, by Ph. J. DE KADT 217

Contributed discussion on " Estimation of Unsaturated Hydrocarbons," by Prof. J. S. S. BRAME 221

Reviews : " A Text Book of Geology," by James Park ; " Oil-Field Exploration and Development," Vol. II., by A. Beeby Thompson ; " Tiefbohrwesen, Forderverfahren und Elektrotechnik in der Erdolindustrie," by L. Steiner 224

CONTENTS.

PAGE

Current Petroleum Notes 232

Ninety-third General Meeting :—

The Oilfields of the Maracaibo Basin, by CAMPBELL M HUNTER, O.B.E., M.A., A.M.Inst.C.E., F.R.G.S., F.G.S. 235

Discussion : Sir FREDERICK W. BLACK, Messrs. D. A. SUTHERLAND and CHARLES DABELL 246

Contributed discussion by Mr. BASIL F. MACRORIE .. 252

Written reply by Mr. CAMPBELL M. HUNTER 254

Ninety-fourth General Meeting :—

Organic Theories of Oil Origin, by ERNEST CLARK .. 257

Discussion : THE PRESIDENT, Prof. V. C. ILLING, Messrs. T. DEWHURST, J. E. HACKFORD and A. BEEBY THOMPSON 278

Reply by Mr. E. CLARK 285

Contributed discussion by Dr. P. E. SPIELMANN.. .. 286

The Physical and Chemical Properties of Paraffin Wax, particularly in the Solid State, by J. A. CARPENTER, M.A., A.I.C. 288

Working Hypotheses in the Geological Search for Oil, by MURRAY STUART, D.Sc., Ph.D., F.G.S., F.C.S. .. 316

The Liability to Explosion of Carburetted Atmospheres in Petroleum and Distillate Storage Tanks, by A. WILLIAMS-GARDNER, B.Sc.(Tech.) 336

Students' Section :—

Electrical Methods of Prospecting for Oil, by J. O. TANNER, B.A.(Cantab.) 341

Reviews : " Les Proprietes Physiques des Vapeurs de Petrole et Les Lois de Leur Ecoulement," by Jean Rey ; " Schlomann-Olenbourg. Illustrated Technical Dictionary. Vol. IV., Internal-Combustion Engines," by Karl Schikore ; " The Oil Industry," by E. R. Lilley ; " Chemical Engineering and Chemical Catalogue," by D. M. Newitt ; " Petroleum-Vademecum. International Petroleum Tables," by R. Schwarz ; " The Lancashire Coalfield : The King Seam," Dept. of Scientific and Industrial Research 347

PAGE		PAGE
232	Current Petroleum Notes	350
	Reports on the Progress of Naphthology during 1925 :—	
235	Oilfield Practice, by A. Beeby Thompson, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S.	351
246	Drilling Methods and Tools, by Ashley Carter,	
252	A.M.I.Mech.E.	361
254	Retortable Oil-Yielding Material, by E. H. Cunningham Craig, B.A., F.R.S.E., F.G.S.	362
	Oil-Shale, by Victor C. Alderson, D.Sc.	366
257	Refining, by J. McConnell Sanders, F.I.C., F.C.S. ..	374
	Developments in American Petroleum Refining, by	
278	Benjamin T. Brooks, Ph.D., F.C.S.	385
285	Cracking, by R. Pitkethly	393
286	Lubricants, by Harold Moore, M.Sc. (Tech.), A.Inst.Mech.E.	403
	Special Products, by F. G. P. Remfry, B.A., D.Sc., A.I.C.	411
288	Analysis and Testing, by S. Bowman, F.I.C.	416
	Oil and Gas Developments in Canada, by G. S. Hume	420
316	British West Indies, by A. P. Catherall, B.Sc., M.I.Min.E., A.M.Inst.M.M.	423
336	Japan, by Toyokichi Takakuwa	429
	The Production of Oil-Shale and Shale-Oil in Estonia, by P. N. Kogerman, M.Sc., D.I.C., F.C.S.	431
341	World's Production of Crude Petroleum, by George Sell	435
	The Structure and Stratigraphy of the North-West Indian Oilfield, by Ernest Parsons, M.Sc., F.G.S.	439
	Contribution to the Knowledge of Polymerisation :—	
	Part I., by H. I. Waterman, Ph.D., and J. N. J. Perquin	506
	Part II., by H. I. Waterman, Ph.D., and J. C. Jamin	510
	The Composition of Petroleum (Kerosene and Other) Fractions, with the Standardization of Miscibility and Optical Tests,	
347	by J. A. Carpenter, M.A., A.I.C.	518

CONTENTS.

PAGE

Torbanite and Its Treatment by the Bergius Method, by Prof. A. W. NASH, M.Sc., F.C.S., M.I.Mech.E... .. 568

Some Experiments on the Oxidation of Lubricating Oils, by HAROLD MOORE, M.Sc.(Tech.), A.Inst.Mech.E., and JAMES BARRETT, A.M.C.T. 582

On the Accuracy of the A.S.T.M. Distillation Method, by the LABORATORY of DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ 586

Students' Section :—

The Main Constituents and Possible Utilisation of Primary Tar, by CHRISTOPHER JOHN WARD 591

Reviews : "Treatise on Sedimentation," by William H. Twenhofel; "The Geology of Oil, Oil-Shale and Coal," by Murray Stuart; "The Theory of Emulsions and Emulsification," by W. Clayton; "Petroleum Development and Technology in 1925," by American Institute of Mining and Metallurgical Engineers; "Power Alcohol Production," by Ministry of Agriculture and Fisheries 598

Ninety-fifth General Meeting :—

The Significance of Surface Oil Indications, by A. BEEBY THOMPSON, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S. 603

Discussion : Messrs. T. DEWHURST, F. G. RAPPOPORT, J. ROMANES, Prof. V. C. ILLING, Dr. ARTHUR WADE, Messrs. H. B. MILNER, CHARLES DABELL and ALEXANDER DUCKHAM 622

Reply by Mr. A. BEEBY THOMPSON 630

Contributed discussion by Mr. I. A. STIGAND 632

Ninety-sixth General Meeting 635

Determination of Benzene in Alcohol Solutions, by W. R. ORMANDY, D.Sc., F.I.C., F.C.S., and E. C. CRAVEN, B.Sc., F.C.S. 636

Further Experiments with the Moore Ignition Meter, by W. R. ORMANDY, D.Sc., F.I.C., F.C.S., and E. C. CRAVEN, B.Sc., F.C.S. 650

Fifth International Road Congress. Report by PERCY EDWIN SPIELMANN, Ph.D., F.I.C. 655

PAGE
568
582
588
591
598
603
622
630
632
635
636
650
655

CONTENTS.

PAGE

American Petroleum Institute. Proposed Projects in Research in Petroleum 659

Students' Section :—

Conditions Governing the Occurrence of Oil in Burma, by L. DUDLEY STAMP, B.A., D.Sc.(Lond.), A.K.C. .. 663

Correspondence 665

Reviews : "The Scientific Principles of Petroleum Technology," by Dr. L. Gurwitsch, translated by Harold Moore ; "Investigation on the Treatment of Nova Scotia Oil Shales," by Prof. A. E. Flynn ; "L'Activite des Volcans de boue en Relation avec la Structure des Plis Gaziferes et quelques arguments contre la migration du Petrole," by Dr. S. Zuber ; "Report of Test on the Fusion Rotary Retort," Dept. of Scientific and Industrial Research ; "Art de l'Engenieur et Metallurgie. Resistance des Materiaux et Donnees Numeriques Diverses," by L. Descroix ; "Report on Heavy-Oil Engine Working Costs (1925-1926)," Diesel Engine Users' Association .. 666

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE EIGHTY-NINTH GENERAL MEETING of the Institution was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, December 8th, 1925, Prof. J. S. S. Brame (Past-President) occupying the chair.

The Secretary read the names of members elected and transferences made, since the previous meeting, as follows :—

Members.—Walter Bernoulli, Herbert George Howson, William John Millard, William Charles Mitchell, Hisahiro Naito, Percy Edwin Spielmann.

Transferred to Member.—Ernest Parsons.

Associate Members.—William A. Peters, John K. Walton.

Transferred to Associate Member.—Douglas Wood.

Students.—George Dickinson, Rogers Garson Ffoulkes-Jones, John Stanislaus Gaynor, George Camille Felix Greant, Charles Frederick Carre Moore, Edward Lionel Moore, Cyril Bloomfield Roach, Hendrik Willem Slotboom.

Associate.—Horace Fleming Smith.

The Chairman then called on Mr. J. H. S. Dickenson to read the following paper :—

The Selection and Properties of Steels used for Oil-Well Boring Equipment.

BY J. H. S. DICKENSON, F.Inst.P., B. GRAY, B.A., and F. E. CHERRY, M.Inst.P.T.

1. INTRODUCTORY.

THE same principles now applied to the choice of material for some highly stressed part of a modern æro engine are precisely those which may, and should, decide the type of steel to be used in a drilling jar, or a fish tail bit.

The difficulty of correlating manufacturing data with actual working behaviour has led to rather more empiricism in the selection of oil well steels than accords with efficiency. Exchange

of data does, however, take place and the frank communication of information concerning the physical characteristics of material, in return for accurate reports on service performance, may benefit driller and metallurgist alike.

There is the costly process by which first one steel and then another is tried until a more or less satisfactory result is obtained, and alternatively the scientific method which assists in the selection of that steel having those physical properties most likely to withstand the working conditions to which some given part is subjected.

The successful application of the latter method depends upon an understanding of the relationship between certain physical properties of steels and ultimate performance under various working conditions ; and also of the effect of variations in composition, and of heat-treatment, on the physical properties of steels.

2. On the Relationship between the Mechanical Properties of Steel and Good Behaviour in Service.

The physical properties required in a piece of steel are those which best enable it to withstand the particular set of destructive influences acting upon it, and so to avoid failure in service.

All cases of failure under stress may be placed in one of three classes as follows :—

1. By deformation.
2. By wear or abrasion.
3. By fracture.

The first class comprises all cases where a part changes shape to an injurious extent. This may be due either to elastic or plastic flow. In the former case the part returns to original shape when stress is removed, in which event nothing can be done but to increase the dimensions, because all steels have much the same " modulus of elasticity " up to their respective elastic limits. This means that if a pull of 10 tons per sq. inch is applied to a long bar, either of mild carbon steel or of a very high tensile nickel chromium steel, it will equally extend to 0·07 per cent. above the original length, a stretch which will disappear completely when the load is removed. If the pull were increased to, say, 20 tons per sq. inch, the mild steel bar would stretch considerably, and remain stretched after unloading, while the other would extend elastically another 0·07 per cent., the " strain " being proportional to the " stress," returning to original length as before when unloaded.

If tensile test pieces were slowly and continuously loaded, the mild steel would be observed to give a sudden stretch at about 15 tons per sq. inch, afterwards stretching quite rapidly until rupture occurred, and the high tensile steel, on the other hand,

would show no such "yield point" until, perhaps, 45 tons per square inch had been applied, when it in turn would cease to stretch elastically, and would exhibit permanent deformation if unloaded before being pulled in two.

Obviously, then, the failure of a steel part by plastic flow is due to the application of stress above the "yield point" of the steel.

In the second class of failure the principal property involved is "hardness." Certainly it is not the sole consideration; undue brittleness must be avoided; but resistance to wear by eroding influences can only be secured if the steel is sufficiently hard.*

It is not yet possible to give a really satisfactory definition of "hardness" or to agree upon a perfect testing method, but in practice the Brinell Test, which measures the impression produced upon a flat surface by a hard steel ball under some given load, is useful and convenient for soft or moderately hard steels.

When the hardness approaches that of an ordinary hard steel ball it is necessary to resort to the diamond indentation test, the diamond scratch test, or the "scleroscope," but in skilled hands a small file or a glass bottle may be made to give very helpful indications of the comparative hardness of cutting edges.

The third class of failure, by fracture, may be conveniently sub-divided as below :—

3a. By rupture in direct tension, torsion, or shear, after preliminary deformation.

3b. By sudden fracture or "snapping" under shock or steady stress, but without preliminary deformation.

3c. By fatigue.

These three sub-divisions vary considerably in importance, and the first type of failure by fracture may be quickly disposed of, as it is simply an extension of the class of failure by plastic deformation, flow having continued until rupture has supervened.

In cases of this kind the physical properties concerned are first the "yield point," where failure virtually commences, and the "maximum stress," when separation occurs.

The next subdivision includes all those cases where failure occurs by sudden cracking, or snapping. The physical property required to reduce this liability is "toughness," and a failure of this type indicates that the steel is not "tough" enough, or conversely that it is too "brittle." It is most important to note that although "toughness" is dependent upon the degree of "ductility," the two properties are dissimilar, and should not be confused.

* Manganese Steel forms a special case which will be mentioned later.

It is found that quite ductile material may be made under certain conditions to break in a very brittle manner, and some steels which give a large stretch in the tensile test, and are obviously ductile, will break readily if notched and struck sharply so that the stress is concentrated at the base of the nick.

Ability to withstand sudden and locally applied stresses of this kind constitutes "toughness," and can only be determined by some type of notched impact test such as the Izod, the Charpy, or the Fremont Tests, each of which measures the energy required to produce rupture across the section of the test piece, general deformation being prevented by the stress-concentrating notch.

It should be observed that, although ductile steels may not be tough, there cannot be toughness without ductility, and that, as the ductility tends to be less as the hardness of a steel is greater, very hard steels can never be very tough. The most to expect is that the toughness of a sample shall be as much as is consonant with the degree of hardness, whatever that is.

The third subdivision of this group comprises all cases of fatigue, the commonest type of failure, which occurs in infinite variety.

"Fatigue flaws," or "creeping cracks" as they are sometimes called, are liable to form at an abrupt change of section, a badly finished fillet, a sharp tool mark, a key-way, or, indeed, any place where stress concentration may occur in a part subjected to continued reversals or repetitions of stress.

Occasionally fatigue flaws develop with very complicated ramifications, and sometimes are not unreasonably mistaken for original defects in the steel, although "growth lines" are usually visible.

Only the merest sketch of the phenomenon of fatigue can be attempted in the present paper, and those wishing to go further into the subject are referred to the book by Gough, on "The Fatigue of Metals," recently published by Scott, Greenwood and Co.

It was once supposed that sudden fracture by fatigue occurred only when the steel had been rendered brittle by general recrystallisation under the influence of vibration, but it is now definitely known that the steel is quite unaltered except in the path of the growing flaw, which proceeds by a process of progressive disintegration along an extremely narrow front.

Steel is built up of an enormous number of minute crystalline grains, and it is their individual behaviour under stress which determines the mechanical properties of the steel as a whole. Each grain is provided with cleavage, or gliding planes, and when a grain is caused to deform by stress, "slip" or lateral displacement occurs at some of these cleavage planes.

This may culminate in actual cleavage across the grain, if repeated a sufficient number of times. When this occurs in the grains at some point on the surface of a forging subjected to unduly severe stress repetitions or reversals, we have the commencement of a fatigue flaw, which grows as the underlying grains are successively ruptured in the same way.

The physical property of the steel which is concerned in resisting fatigue is the range of stress through which the steel may be indefinitely reversed without causing destructive slip at the crystalline gliding planes. This is, indeed, the true elastic limit of the steel, not as determined by the "limit of proportionality," or the "yield point," in the tensile test, but by some modification of the "Wohler test," in which a test bar is subjected to repeated stress cycles of known range until breakdown.

Although, in most cases, liability to fatigue at a highly stressed place in some given part is lessened, or entirely removed, by the use of steel having a higher fatigue range, there are certain important exceptions to this rule. These are the cases where such exceedingly severe repeated stresses are thrown upon a forging, that sooner or later fracture is inevitable.

It is then found that the use of a softer steel, with a relatively small fatigue range, leads to longer life, probably because the greater ductility permits more surface yielding at the highly stressed place and thus tends to distribute the stress, while the correspondingly increased toughness is of importance in increasing the work of rupture expended as fatigue proceeds.

In some border line cases it becomes a difficult problem to decide whether the repeated fatigue failure of a part should be met by using a softer steel, to prolong life, or a harder steel to eliminate fatigue altogether. Such a case has been provided by drilling jars which have been found to give the best results on one field when made of steel with reduced fatigue resistance and increased toughness, but on other fields when heat-treated to enhance the one property and reduce the other.

3. On the Influence of Composition and Heat-treatment on the Mechanical Properties of Steel.

The mechanical properties of a piece of steel depend primarily on the proportions and structural arrangements of the microcrystalline constituents of which it is composed.

The science of Metallography names the various types of crystalline grain "Martensite," "Troostite," "Pearlite," and so on, but such technicalities are outside the scope of the present paper, and the authors have, accordingly, attempted in the present

section the somewhat formidable task of explaining in a simple manner how the varied mechanical properties of steels are to be obtained.

Steel is built up of crystalline grains which vary in size, according to the heat treatment, the grains composing an average bar of mild steel having a diameter of about 0·003 in., there being roughly 30 millions of them in a cubic inch.

The same volume of a fine grained tool steel will contain many hundreds or thousands of millions, while a badly overheated steel may be built up of relatively huge grains, as much as 0·03 in. across and with only about 30,000 in a cubic inch.

A bar of pure iron is composed of only one kind of grain, each an internally perfect crystal of iron, and remains soft, ductile, tough, and low in fatigue resistance after any form of heat-treatment.

Steel, on the other hand, contains at least two very different constituents, one being soft pure iron, and the other very hard iron carbide. When other elements are added, such as manganese, chromium, nickel, etc., the completely crystallised cold steel still contains only two ultimate constituents, one relatively soft, the other very hard, but instead of pure iron the former is a solid solution, as for example, of nickel and silicon in iron, and the latter a complex carbide, such as that of iron and chromium, instead of simple iron carbide.

Leaving on one side the impurities steel may contain, we may take it that a cold solidified ingot of steel contains two essential constituents, one relatively soft, the other very hard. Now if these two components, having once separated, were immovable and incapable of re-arrangement, the engineer would be without the wonderful variety of special steels now at his disposal. Fortunately it is only necessary to heat the steel to a red heat ; when a " critical change " occurs, and the two constituents mutually diffuse to form what is known as a solid solution. This change takes time and involves the absorption of heat, but when complete at, for example, 760° C. in an ordinary 0·60 per cent. carbon steel bit, the steel is entirely composed of one kind of internally homogeneous crystalline grain.

If, now, the steel is reduced to the atmospheric temperature, the mechanical properties will depend on the manner in which the two constituents re-arrange themselves if, and as, they separate from the solid solution.

Suppose that on cooling down a hard steel containing 1·2 per cent. carbon (*i.e.*, a typical file steel), the hard carbide not only separated completely, but coalesced into large spheroids, say, the size of duck shot, each well spaced from its neighbours in a matrix of soft iron. Clearly a bar having a structure of this

kind would behave under stress almost exactly like soft iron, the carbide present having a negligible stiffening effect.

Now although separation never proceeds to this extreme, the dissolved carbide does, in fact, separate very completely, if afforded sufficient time, as the steel cools through a "critical change," which is an exact reversal of that which occurs on heating.

In some special cases, the separated carbide may even coalesce to form minute globules, which although very hard, do little to prevent deformation in the surrounding iron, and therefore such a structure implies much ductility, a low yield point, and maximum stress, and little more resistance to fatigue than is offered by soft iron itself.

Now unless softness, and nothing else, is wanted, such a structure is seldom useful to the engineer, and we may go to the other extreme, and see what happens when the breakdown of the solid solution is hindered.

Suppose a piece of 0·60 per cent. carbon steel, *i.e.*, a typical bit steel, at a temperature of 800° C., the carbide being in homogeneous solid solution, is *instantaneously* quenched out and rendered cold. The result would be softness, the consequence of having completely suppressed any separation of carbide whatever, and the steel would remain in the cold a greatly undercooled solid solution, with much ductility, low fatigue resistance, but, probably, with a marked tendency to work-harden, like manganese steel.

Let us next, having overshot the mark, proceed to a less drastic and much more useful treatment, and quench the sample in cold water, which has a rapid, but far from instantaneous, cooling effect.

The solid solution would then have time for some slight breakdown, but long before this could be completed the steel would be cold and so rigid that further separation of carbide would be impossible.

The result would then be extreme hardness, coupled with little or no ductility and a marked tendency towards brittleness, while the microscope would reveal little crystalline structure and no visible separated carbide.

The degree of hardness produced by interference with the critical change on cooling varies over a wide range, and depends on three principal factors, these being :—

(*a*) The cooling rate when quenching, which depends on the medium used and the mass of the part quenched.
(*b*) The percentage of carbon.
(*c*) The presence of additional elements such as manganese, nickel, or chromium, which make the solid solution more stable, and thus make any given quenching rate more effective in suppressing the carbide separation.

The practical use to be made of the opportunities thus presented may now be considered in relation to two distinctly different types of heat treatment.

The first use to be made of hardness as produced by quenching is the provision of hard cutting edges of every kind, of hard surfaces on roller races, etc.

The second is hardly less important because the nearly homogeneous condition of the steel provides a preliminary phase in the production of a steel having a valuable combination of mechanical properties.

As regards cutting edges generally, and particularly those of drilling bits, we are not much dependent on the third factor because the cooling rate which can be produced at a projecting edge by water quenching is usually more than sufficient to produce all the hardness required if sufficient carbon is present.*

It is a different problem when we come to deal with the production of hard surfaces, as opposed to cutting edges, because the rate at which heat can be abstracted from the hot steel, and, therefore, the extent to which the critical change on cooling is suppressed, depends not only on the quenching medium used, but on the shape and dimensions of the steel immersed.

Consequently it is necessary to call in the aid of the third factor when deep hardening is required, and use a steel containing not only fairly high carbon, but some chromium or another element having a similar effect. This addition causes more "intensive" hardening than can be obtained by carbon alone, so that the quenching "strikes deeper."

The deeper hardening thus obtained is sometimes useful in cutting edges, very important in obtaining uniformly hardened rollers, dies, etc., but is absolutely essential in the heat-treatment of the so-called "high tensile" steels, and so we arrive naturally at the second use to be made of the structural condition associated with hardness.

We have found that a steel can be made either very hard, and structurally very homogeneous, or very soft, with the carbide well and freely separated, according to whether the critical change is hindered or assisted.

The one condition gives, in greater or less degree, hardness, a high resistance to fatigue, and very little toughness.

From the other is obtained softness, ductility, more or less toughness, and weakness in resisting fatigue.

---

* We are not considering here the special case of tools which are required to cut metals at such high speeds that the cutting edge is considerably heated and special elements such as chromium and tungsten are added, primarily with the object of obtaining "red-hardness."

Steel required to resist both fatiguing stresses and heavy shocks must, however, have both a high fatigue limit and much toughness, a combination which can only be secured by distributing the carbide throughout the iron in the form of very minute but structurally free particles.

In practice this is effected by first hardening the steel so as to produce the homogeneous structure, and then by " tempering."

Tempering means heating to some suitable temperature *below* the change point, and begins to take effect in most fully hardened steels below 200° C. It results, as the temperature rises, in a progressive separation of more and more of the finely divided carbide, this being manifested in mechanical tests by a continuous fall in hardness and corresponding increase in ductility.

When the critical range is reached the separated carbide again passes into solution, and the cycle is complete, but actually tempering should never be taken higher than about 30° C. below the lower limit of the critical range.

The wide range of mechanical properties made available by variations in the tempering heat is very useful in suiting special conditions, but the best all-round temperature for the usual alloy steels may be taken as 600° to 650°, when practically all the carbide has separated in minute, almost ultra microscopic plates scattered through the ground mass of relatively soft free ferrite.

Such a structure provides ductility, toughness, and a high elastic limit, with which may be coupled high fatigue resistance.

This, then, is the condition which is to be found in any correctly heat-treated " high tensile " alloy steel, such as a typical nickel chromium steel which is capable of giving an elastic limit five times that of pure iron, with at least equal toughness, if not so much ductility.

To get this highly advantageous structure by heat-treatment there are two principal essentials, the first being that there must be just about the correct amount of carbon in the steel to provide sufficient stiffening carbide without unduly breaking the continuity of the soft ferrite in the tempered steel, and the second, that any part, large or small, shall be effectively hardened throughout.

For parts of any mass this necessity compels recourse to the third factor, and special elements such as nickel and chromium must be added with the object of slowing down the critical change on cooling, and so making a milder and more equable quenching than that of water, effective in producing the desired homogeneous structure and hardness. It is quite unnecessary for the purpose that a high degree of hardness should be produced, only that it should give the required structure and be uniform, and it is possible by the use of sufficient nickel and chromium together, to produce

steels capable of hardening uniformly throughout when cooled from 820° C. in still air, or at even lower rates.

A more generally useful class of "high tensile" steels, containing about 0·30 per cent. carbon, 3·50 per cent. nickel, and 0·60 per cent. chromium, when quenched out in oil will harden uniformly throughout quite large masses, so that subsequent tempering produces everywhere a high combination of mechanical properties, only to be obtained from carbon steel when quite small bars are water quenched and tempered.

Intermediate results may be obtained from steels containing either nickel or chromium separately, although much depends on the mass of the part treated.

Before closing this section some reference should be made to the fact that the great bulk of structural steels are not required to have anything like the mechanical properties of the steels just discussed and that simple cooling in air after rolling or forging—or after the simple heat-treatment of "normalising"* when special uniformity is required—leaves the carbide in a sufficiently scattered form to give an adequate elastic limit, and enough toughness. All such steels are "pearlitic," built up of two distinct kinds of grain in proportions depending on the carbon content, some being pure soft iron, while the others, the pearlite grains, are composite in structure and contain all the carbide in the form of lamellæ. This natural structure of carbon steels may be made to give improved mechanical properties, if still far short of the heat-treated alloy steels, by water or oil-hardening and tempering, which distributes the carbide to some extent and produces what is known as the sorbitic structure.

Limitations of time and space render it necessary to pass on to consider the special requirements of oil-well steels, leaving unmentioned many matters of interest and importance.

4. On Oil-Well Steels, in the Light of the Foregoing Sections.

A systematic selection of the most useful and appropriate steel for each of the more important oil well parts may be conveniently based on Table I., which shows the types of failure to which each part is more particularly liable.

This table assumes that reasonably suitable steel is used, as obviously the types of failure to which any part is liable would be increased in number, as well as aggravated, by the use of patently inappropriate material, very faulty design having a similar effect.

* "Normalising" means heating a piece of steel to a few degrees above the upper limit of the critical range, followed by cooling in still air.

The parts tabulated are confined to those used in the standard percussion and rotary systems of drilling, but amongst these is a counterpart to almost every important tool, or steel part, used in other methods.

Before proceeding to discuss in some detail the various parts scheduled, the table may be conveniently considered in a general manner.

TABLE I.

Manner of Failure.

Steel part.	By deformation without fracture.		Wear or abrasion	By fracture.		
	Elastic	Plastic.		By rupture after deformation.	By sudden fracture by snapping.	By fatigue.
Bit	—	Flow at cutting edge.	Wear on cutting edge.	—	Pin in making up. Flaking of cutting edge	Pin through whipping of drilling stem
Jars ..	—	Flow at cutting edge.	Abrasion on reins	—	Reins through excessive drilling shocks.	Reins & pins by repetition drilling stresses.
Under-reamer cutters		Flow at shanks and cutting edge	Wear on cutting edge.	—	Shank throu' excessive drilling shocks.	Shank by repetition drilling stresses.
Slips ..	—	Crushing of teeth.	—	—	—	—
Chains ..	—	Stretched links.	Abrasion by grit.	—	—	—
Sprockets ..	—	Flow on teeth.	Abrasion by grit.	—	—	—
Roller bits ..	—	—	Wear on working surface	—	Chipping of edges.	—
Tool joints ..	—	Flow at threads.	Wear at threads.	—	—	—
Wire line sheaves	—	—	Wear by slipping	—	Cast iron only	—
Working barrels and plungers	—	—	Abrasion by sand	—	—	—
Sucker rods..	Stretch	—	Wear by rubbing	—	—	At weakened places.
Percussion drill stem	—	—	—	—	Vicinity of welds, by drilling shocks.	At changes of section, pins and weld flaws.
Drill pipe ..	—	—	—	By twisting.	By torsional shock.	Repetition stresses (torsional).
Casing ..	—	Collapse.	—	Under own weight.	—	—
Wire lines ..	—	Stretch.	Abrasion by grit.	Of individual strands.	Of individual strands.	Of individual strands.

In the first place it is perfectly clear, as might indeed be expected, that resistance to wear at some place or other is required in most cases, and that quite frequently this requirement, which calls for hardness, is coupled with the necessity for toughness to resist sudden fracture by snapping. These dissimilar, and opposed, physical characteristics are required in some cases in different parts of the same forging, and can be obtained by differential heat-treatment. In others, as in the case of the drilling jar, it is necessary to have either at the same point or within a relatively limited area, a combination of high elastic limit in order to resist both wear and fatigue stresses, as well as much toughness to avoid sudden fracture by snapping. Here it is impossible to employ differential heat-treatmefit in the full sense of the word, but fortunately suitable alloy steels, heat-treated on the lines described towards the end of the last section, are available and prove very satisfactory. In other cases again, such as slips, easy deformation in the steel as a whole is a virtue rather than a fault, except at the ends of the teeth, where great local hardness is required and can best be produced by a special form of differential treatment, that is to say by case-hardening.

Bits.—It is indicated by Table I. that the cutting edges of a bit must be hard in order to resist deformation and wear, but that at the pin the steel must have toughness sufficient to avoid fracture either under heavy shocks, or lighter repetition stresses.

The necessity for so much toughness at the pin would probably not be so great if the joint could be made without causing irregular stresses at the screw threads, or at the base of pin, but in practice this is unavoidable and quite frequently the stress concentration on one side is such as to cause the pin to jump off the first time the jack is used on it.

Any failure to make the faces of the joint meet also results in stress concentration at the base of the gap, no matter how narrow, and this is likely to lead to failure by fatigue, sooner or later, particularly in percussion drilling.

These conditions are best met by a high degree of toughness and ductility, high fatigue resistance being a secondary consideration, and the problem is to secure such a physical state at one end of the forging and great hardness at the other. Until comparatively recently the constant trouble with pin failure was countered by the welding of a wrought iron or mild steel pin on to the hard steel of the bit proper. Welded pins are still insisted upon by some users, but really there is no need for them, as the cause of the trouble with the pins of all-steel bits was due either to the use of an unsuitable steel, or to faulty heat-treatment, which may be taken to include no heat-treatment at all. In the latter event

the steel at the pin may be small grained or large grained, tough or brittle, according to the temperature at which the forging leaves the hammer, an irregularity which cooling in ashes or lime—a very undesirable practice when applied to bits—does little or nothing to eliminate.

Provided that an all-steel bit is properly annealed after forging, it is possible to get quite adequate toughness at the pin end from harder steel than is necessary to provide good cutting edges, or than is rendered desirable by the exigencies of field heat-treatment. This introduces a very important factor in the selection of the best bit steel because the chances of splintering or cracking during hardening, splitting when dressing, or internal cracking by unequal expansion when re-heating, are all enhanced as the carbon content of the steel increases, the danger being intensified by the presence of special additions such as chromium.

When very hard tools are dressed and hardened by high-skilled men, using the best types of furnaces, these defects, which are caused by too rapid or irregular heating, unduly high temperatures, or improper quenching conditions, can be reduced to a minimum.

Such a standard cannot reasonably be expected on the field, so that lower carbon steel must be used than would otherwise be selected to give the best results in service, while alloy bit steels can only be considered safe when the field heat-treatment is carefully watched. At the same time there is no doubt that quite unnecessarily "soft" steel is largely supplied for use on oilfields, not only because the manufacturer is less likely to receive complaints about cracking, for which the steel and not the treatment is blamed, but also because less care is required in the preliminary annealing to avoid brittleness at the pin.

The loss of efficiency thus occasioned is very considerable, as was proved by alternate drilling with fish-tail bits containing 0·65 per cent and 0·55 per cent. carbon, when the former made on the average 20 per cent. more hole without re-dressing.

As careful annealing will give ample toughness at the pin with much more carbon than 0·65 per cent., the object in the choice of a bit steel should be to get as much hardness at the cutting edges as is consonant with immunity from chipping or flaking in service and reasonable ease in field dressing and hardening.

In most cases the depth of hardening obtained from plain carbon steel is quite adequate, and there is little or no advantage to be gained by the use of alloys, except possibly in fish-tail bits and small percussion bits, when chromium may be used if fairly efficient tool dressers are available.

When chromium is used the carbon should be lowered a little so that the surface or edge hardness will be much the same as with

ordinary carbon bit steel, but the hardening strikes deeper and more work can be done before the underlying softer layers are reached, the tool becomes inefficient, and re-dressing is necessary.

The danger of internal cracking, or "clinking" through unequal heating, becomes greater as the mass of the tool increases, and must be compensated for by the use of lower carbon steel, so that taking all factors into account the following are considered by the authors to be the most suitable compositions for the types of bit indicated :—

TABLE II.

	Carbon. Per cent.		Silicon. Per cent.	Manganese. Per cent.	Chromium. Per cent.	Upper Limit of critical range.
	Min.	Max.	Approx.	Approx.	Approx.	° C.
Fishtail bits and small percussion bits ..	0·65	0·70	0·15	0·50	—	750
Medium percussion bits and four-winged bits	0·60	0·65	0·15	0·50	—	760
Large percussion bits.	0·55	0·60	0·15	0·50	—	770
Chromium steel for fish tail bits	0·50	0·55	0·15	0·50	0·60	780

The actual treatment and manipulation of a forged bit may now be shortly considered.

After forging a bit should be rendered uniformly ductile and tough throughout either by heating to 820° C. (just above the critical range) and then slowly cooling, or better by first oilhardening as a whole and then reheating to about 710° C., when the change point is just reached.

The latter method has the advantage that the steel is not only completely softened, but is left with the carbide well distributed so that it is tougher than when distinct ferrite and pearlite grains are formed.

The next operation of hardening depends for success upon a series of factors.

The end of the bit should not be charged direct into a hot fire of any kind without some preliminary warming or otherwise great internal stress may be set up by irregular expansion, and cause "clinking."

This means that at some point, usually well below the surface, but sometimes on the surface, the direct stresses set up by irregular expansion actually rupture the steel, and the crack so started may extend completely across or along the forging. Not infrequently the steel itself is undeservedly blamed for this happening.

The edges should then be raised uniformly, and fairly slowly, care being taken that the temperature gradient into the colder body of the tool is not too abrupt, to the hardening temperature. This should be the lowest possible, as every degree in excess leads

to increased grain size, more risk of cracking during quenching and greater liability to chipping in use.

The lowest temperature theoretically possible is, of course, the upper limit of the critical range, as indicated for each type of bit steel in Table II., but a practical margin must be allowed, and gives a working temperature of 790° C. to 810° C.

There are several workshop methods besides the use of pyrometers by which this exceedingly important temperature—too often loosely described as a "low red heat" or "cherry red"—may be checked. One suggested method is by the use of a magnet, because steels of this type very conveniently lose their magnetism at the carbon change point, but the very serious practical disadvantage of this method is that very little heating is required to rob the magnet of its own attractive power and so make the test more impressive than helpful. A much more useful expedient is to scatter a little common salt on the hot cutting edge. This melts sharply at 800° C., when it is easily observed to glaze, or take a wet appearance, and the steel is ready for quenching, of course if it is uniformly heated.

This achieved, the bit should be removed from the furnace and immersed to a depth of three or four inches in clean water. The quenching pan is conveniently provided with a grid on which the bit may rest, the level of the water being regulated at the correct depth.

Fish-tail bits should not be immersed to cover the angle between the wings or otherwise a bad hardening crack may form.

When it is found that a consignment of steel proves too hard after water-quenching, oil may be substituted for quenching, but in the hands of a really good smith a better modified treatment is to temper the water-hardened bit by early withdrawal from the bosh, exactly as in the case of a cold chisel.

When redressing becomes necessary, it is again imperative to avoid abrupt and irregular heating, but as the temperature now to be obtained is higher than that required for hardening, there are additional dangers to be guarded against. The first of these is "decarbonisation," or the removal of carbon from the heated surface of the steel by oxidizing furnace gases. If the steel is kept for long at a high temperature in a "cutting" flame, the whole of the surface carbon may be removed so that after quenching the cutting edges are soft and inefficient.

The second is "burning," when oxygen from the furnace gases actually passes into the steel to form membranes of oxide round the crystalline grains, with extreme brittleness as a consequence. Burnt steel is usually fit for nothing but the melting furnace, but without reaching such an extreme degree of overheating the steel

may be seriously injured if the forging or dressing temperature is unduly high. It has already been pointed out that after the critical change has been passed, at 740° C., the grain size continually increases, but on the other hand forging, or otherwise working the steel after it leaves the fire, keeps the heated steel continuously broken up and consequently the ultimate grain size in forged steel depends on the temperature at which forging ceases.

If the steel is made very hot and only worked a little, so that it is laid down to cool from a high temperature, the grains may be so coarse that they are not properly broken up by the subsequent reheating for hardening, and brittle edges result, although the hardening has been properly carried out.

If, on the other hand, the steel is heated to the lowest temperature consistent with reasonable plasticity in dressing, and is then hammered until the temperature has fallen to just a little above the change point on cooling, say 700° C., the effect will be actually to improve the condition of the steel at the cutting edges.

It is very difficult to lay down any definite dressing temperature, for one thing furnace conditions may vary so much, but it should never exceed 1050° C., a bright red heat with a touch of yellow in it, and may advantageously be much lower.

As regards the actual dressing operation, it is most important to avoid the formation of laps or folds, which may lead to "water-cracks" in hardening. Many a fish tail bit has been ruined by a lap formed in the angle between the wings having caused a split up the middle.

There should be a smooth valley, so to say, between the two wings, with not even a sharp Vee groove, much less a fold.

The same thing applies, perhaps to a less degree, to percussion bits, and the surplus material forged back into the watercourse during dressing, should be cut away.

The hardening of the bit after dressing should, of course, proceed on the same lines as after the first forging.

Jars.—The conditions which have to be met by the steel in jars include each of those described in connection with bits, but occur in such a way that the method of differential heat-treatment between the striking end and the pin of the bit is not available to meet them.

The first consideration in these tools is to avoid failure by fracture, failure by wear and plastic deformation being of secondary importance.

In the early days of the industry, jars were made of iron, and with the light tools then in use gave fairly satisfactory, though short, service, because although conditions conducive to fatigue

were undoubtedly present, the actual commencement of the fatigue flaw was so delayed, owing to the great ductility of the material, that failure through wear and plastic flow took place first.

The modern welded jar, which consists of mild steel ends and comparatively hard reins, usually containing about 0·50 per cent. carbon, is undoubtedly a big improvement on the iron jar, when welded by a highly skilled smith, but the difficulty in making a satisfactory weld, and the risk of failure by fatigue or shock, owing to the lesser degree of ductility and toughness is materially increased by the use of such steel in place of iron.

The recent development of the weldless jar has made possible the use of heat-treated alloy steels, hitherto debarred owing to the great difficulty in welding a steel containing sufficient alloys to be really effective in improving the physical properties.

Considerable success has been achieved by several makers using various compositions, all of which, so far as the authors know, contain nickel and chromium in varying proportions, whose functions, as previously described, are to enhance greatly the effect of heat-treatment.

Probably the most satisfactory steel for the purpose has a composition conforming fairly closely to the B.E.S.A. specification S.11, this being :—

Carbon	.. ..	Between 0·25% and 0·35%.
Silicon	.. ..	Not more than 0·30%.
Manganese	..	Between 0·45% and 0·70%.
Sulphur	.. ..	Not more than 0·05%.
Phosphorus	..	Not more than 0·05%.
Nickel	.. ..	Between 3·00% and 3·75%.
Chromium	..	Between 0·50% and 1·00%.

This steel is suggested with confidence, but it is more difficult to prescribe the best condition.

As already stated, jars provide one of those border-line problems where it becomes a question whether failure by fatigue under repeated stress can be obviated altogether by using a hard steel, or whether, ultimate failure being inevitable, all that can be hoped for is to prolong life as much as possible.

There is ample evidence that the former method is possible on many fields ; a high tensile nickel-chrome weldless jar used in the Houston district, Texas, which has drilled over 30,000 ft., being one of many examples. On the other hand, there are fields (notorious to jar makers), where this is far from being the case, and it becomes necessary to use a tough and ductile steel of lower elastic limit and to accept ultimate failure as inevitable.

If this were the whole problem the matter would be comparatively simple, but it is also necessary to retard failure due to wear

and flow at the striking faces as long as possible, which can only be done by raising the yield point.

The physical properties of the steel must, in fact, be a compromise, providing just sufficient ductility to avoid failure by fatigue in the reins before the heads of the jars are so shortened by flow, due to the hammering action, that they are no longer safe.

A wide range is offered by variations in the heat-treatment of the nickel chromium steel of analysis just stated.

Typical test results obtained from this steel after the treatment indicated in each case are given in Table III., and it is suggested that No. 1 is suitable for an all round jar, No. 2 for use on a field where the drilling condtions are very severe, so that resistance to wear has to be sacrificed, to some extent, for the sake of great toughness, while No. 3 has the mechanical properties giving the longest life under good conditions.

TABLE III.

	No. 1.	No. 2.	No. 3.
Yield point, tons per sq. in.	57	45	72
Maximum stress, tons per sq. in. ..	65	55	85
Elongation on 2 in., per cent. ..	20	25	15
Reduction of area, per cent.	60	67	50
Izod impact test, ft. lb.	50	70	20
Brinell hardness number	311	262	385

These are to be taken as typical test results, and not specification figures, which must always allow a working margin.

Under-Reamer Cutters.—The most suitable steel used for these cutters is that prescribed for medium percussion bits on page 7, and everything said about the treatment of bits applies with equal force to these parts.

It is very essential that the shank should be carefully heat-treated so as to obtain the maximum of ductility and toughness, as in the case of the pins of bits.

Slips.—Although slips vary in type they are alike in calling for very hard teeth on a soft and ductile body.

Even supposing that a hard steel was suitable for the body—to make it sufficiently soft and tough would demand even more careful annealing than required for the pins of bits—the local heating and quenching of the teeth would present great practical difficulties. Recourse is, therefore, made to casehardening, the well known process by which carbon is locally absorbed where desired, so that on quenching the carbonised areas are fully hardened on the surface, while the remainder of the body is relatively very soft and tough.

The final toughness of the quenched body depends, however, on

the carbon content of the original steel which should not exceed 0·20 per cent. when the teeth are heavily carbonised to a depth of, say, $\frac{1}{32}$ in., by cementation within a box, but may usefully be higher, say 0·20 per cent. to 0·25 per cent., if the very common practice of "potashing," which produces very superficial hardening, is employed.

Drive Chains and Sprockets.—The links of a drive chain should always be sufficiently strong to resist deformation, and tough enough to avoid fracture if made of an ordinary mild steel, although for heavily loaded chains a rather higher carbon steel, say 0·30 per cent. carbon, may be required, and this should be either normalised, or in extreme cases oil-hardened and tempered.

The pin rollers have to resist both wear by abrasion, and distortion under load, and are most conveniently made by the case-hardening of a low carbon steel.

For sprockets cast iron provides a better wearing surface than mild steel castings, and may advantageously be used where, as in percussion rigs, the stresses are not too high.

An interesting development is the introduction of 13 per cent. manganese steel chains and sprockets, which appears to have some advantages for oilfield work.

This steel is actually softened and toughened by being quenched out in cold water from a high temperature, and is then extremely tough and difficult to break, although it resists certain kinds of abrasive wear to a remarkable degree. Although initially the surface is comparatively soft, this steel becomes locally very hard at any point where cold working or deformation has taken place. It will be seen at once that this feature may be of great value in such parts as those under discussion, since the bearing surfaces will deform slightly, but in doing so, will harden up to such a degree that wear will be greatly reduced. Unfortunately, on account of this very property the steel is impossible to machine, because although the tool will make a start, the steel will immediately harden up in front of it, causing very rapid failure of the tool. The difficulty in manufacture is to obtain the necessary accuracy of dimensions, while, it should be added, manganese steel chains should only be used with sprockets of the same material.

Sucker Rods.—While wear plays an important part, especially when rods are accidently bent and rub against the tubing, the main requirement in a sucker rod is to avoid fracture by fatigue.

There is very little liability to serious shock stresses, so that really high tensile steel giving great resistance both to wear and fatigue could be used except for the necessity of machining screw threads.

In actual fact such hardness would not be much use as regards wear unless the tube were made equally hard, so that the problem becomes to provide a machinable steel of high fatigue resistance.

According to Uren,* the total stress on the upper ends of 1 in. diameter rods in a well 4000 ft. deep, may be over fifteen tons per sq. inch.

Such rods, if made of untreated mild steel, would be stressed almost up to their elastic limit at every up stroke of the pump, and on every down stroke the stress would fall almost to zero, conditions so conducive to failure by fatigue that any slight local concentration of stress, due to some such cause as a defect in the steel, a bruise or kink caused by faulty handling, and so on, will form the starting point of a fatigue flaw.

If the same rods are used in deeper wells failures will be continuous, but the remedy is obvious.

The elastic limit of the steel must be raised, or the section of the rods increased, the latter remedy being only applicable to a limited extent, for the very good reason that a large proportion of the stress is due to the weight of the rods themselves.

It is, therefore, recommended that while ordinary mild steel is quite adequate for shallow wells, the fatigue resistance of the rods for deep wells should be increased by raising the elastic limit. This can be done to some extent by merely raising the carbon content and normalising the rods, but a much higher elastic limit coupled with even more toughness is obtained by oil hardening and tempering a medium carbon steel. The following are typical test results of these three classes.

TABLE IV.

	Mild steel as rolled.	Medium steel normalised.	Medium steel oil-treated
Yield point, tons per sq. in.	15	22	32
Maximum stress, tons per sq. in. ..	29	44	50
Elongation, per cent. on 2 in... ..	37	27	24
Reduction of area, per cent.	65	55	60
Izod impact test, ft. lb.	50	25	30
Brinell hardness number	131	192	223

Up to the present the need for still higher fatigue resistance, such as is obtainable from treated alloy steels, has not arisen, but in any case such material presents no greater resistance to elastic deformation, an important question with the sucker rods of deep wells.

In such wells, sucker rods of too small diameter may prove inefficient through overstressing within the elastic range, the length

* *The Oil and Gas Journal*, Oct. 1, 1925.

of the string being so great that a large proportion of the stroke is lost, due to the difference in the elastic strain in the rods on the upward and downward strokes.

In fact the whole system acts like a long spring, which, indeed, it is. No change in the composition of the steel or its condition is of any avail, as all steels behave alike under stress up to their respective elastic limits, in other words they all have much the same modulus of elasticity, and the only remedy is to increase the section.

It is, perhaps, useful to point out that although all steels are alike in this respect, no other available metal equally resists elastic stretch under load.

Roller Bits.—The bits for these tools usually fail through wear, but because they are comparatively small, and, therefore, more easily handled during forging and treatment the hardness can be greater than that of an ordinary bit, especially as they are usually treated by the maker under good conditions.

Owing to the smaller mass and more rapid cooling during quenching, this increased hardness can be obtained from the same steel as that used for ordinary bits, ranging from 0·50 per cent. to 0·70 per cent. carbon according to the size.

Rotary Tool Joints.—These have to stand a certain amount of direct stress, though this is not very serious, since the drill-pipe to which they are coupled is materially weaker. The chief source of trouble is wear and distortion of the threads owing to the frequent making up and breaking down. It is the practice of many firms to potash or case-harden tool joints after machining and this certainly increases the life. Some distortion of the thread inevitably results from the quenching, and in view of the great importance of accuracy of the thread the process would hardly seem justified. A satisfactory steel to use contains from 0·30 per cent. to 0·40 per cent. carbon, and the forgings should be normalised.

Wire Line Sheaves.—Like chains and sprockets, this is an excellent application for Manganese Steel, as it is of considerable importance to the life of the wire line that the grooves should remain true to shape. Of the more usual materials, cast iron resists the wear of the rope better than cast steel, but it is easily broken under heavy loads.

Working Barrels and Plungers.—For comparatively shallow wells, these are usually made of solid drawn mild steel. A great improvement can be made in their resistance to wear by using a higher carbon steel, containing 0·30 per cent. carbon, or even more. Solid drawn tube of this composition is somewhat more difficult to obtain, since most tube manufacturers have their draw benches

adjusted for mild steel, and the alterations necessary to produce the harder tube involve a serious interference with output. A number of firms, however, can produce such tubes now, and their use is strongly recommended.

For deeper wells, greater accuracy is required than that afforded by solid drawn tubing, and both plunger and working barrel must be ground true. In the case of the plunger, this is a simple operation and requires no comment, but the barrel must have a built up liner of short tubes which can be ground separately. These are best made from cast iron, as the breaking stresses are negligible, and this material wears very well.

Auger Stems.—These parts are, of course, subjected to the same stresses as the pin end of the bit, but as the steel is nowhere required to resist abrasion, the problem is simpler because lower carbon steel may be used.

Formerly they were all made with the ends welded on, but it is becoming increasingly the practice to "head up" the ends in a forging machine from the solid bar. There is no doubt about the improvement, since a weld, however skilfully made, is always a source of weakness for two principal reasons. For one thing it is seldom completely welded over the whole surface, and may cause fracture under sudden shock or by fatigue where stress concentration is set up at weld flaws, either external or internal. There is also the damage often inflicted on the steel in the vicinity, which may be made so coarse grained and brittle by the welding heat that fracture not uncommonly occurs a little way from the weld line, across a zone where there was no subsequent hammering to break down the coarse crystalline grains, as happens at the weld.

For these reasons the weldless stem is much to be preferred, and may be made of steel containing about 0·25 per cent. to 0·35 per cent. carbon, normalised after forging. Lower carbon steel will give little or no longer life, and the threads of the joints will give out much sooner, while with higher carbon the steel is less ductile, with consequently increased liability to failure by fracture.

Drill-pipe.—It is still claimed by many makers that iron is the best material, and where working conditions are not severe and the iron is of good quality it is quite satisfactory.

With deeper wells, more powerful rotaries, and faster drilling, something better is required to resist fatigue, principally occurring at the screw threads.

In these cases the range and frequency of the stress repetition is of such a character that high fatigue resistance is of more importance than ductility and toughness, reversing the case of percussion pin failures by fatigue, and consequently the carbon content used

has been gradually raised until steel containing 0·50 per cent. carbon is now frequently used, when the elastic limit appears to be sufficiently high in the rolled or normalised state to avoid frequent fatigue failure under present conditions.

Any further increase in stress due to faster drilling will have to be met by the use of special heat-treatment, or even the use of alloys, as it would be inadvisable to increase the carbon content beyond 0·50 per cent.

Somewhat paradoxically, it has been found in some cases that liability to fatigue has been diminished by using lighter sections, but of the same steel, probably because general elastic deformation can occur and lessen localised stressing.

Casing.—This has to withstand direct stress longitudinally, and collapsing pressures from the earth or gas. The composition is fixed, at all events for the larger sizes, by the fact that they have to be made by welding, and a low carbon steel is necessary to secure good and easy welding.

Weldless steel casing can now, however, be produced up to 16 in. diameter, which permits the use of higher carbon steel having correspondingly increased yield point and maximum stress. The reduction of section thus permitted allows proportionately greater lengths to be handled, with equal resistance to collapsing pressures.

5. Concluding Remarks.

It is hoped that the foregoing section will sufficiently indicate how the principles previously laid down may be applied to other parts not specifically dealt with.

The paper is not in any sense a schedule, either of steels, or of steel parts, but if members care to bring forward for discussion any unmentioned applications of steel in oil-well equipment, the authors will gladly attempt to deal with them.

It may, perhaps, be also pointed out that the list of special steels grows continually, and that besides the "high tensile" steels of various types and the special abrasion resisting materials, such as manganese steel, there are now available to the engineer several different corrosion or acid resisting steels, the so-called "stainless" steels, as well as the "heat-resisting" alloys, which do not scale appreciably and remain remarkably strong at high temperatures.

These very interesting and valuable steels are, perhaps, not likely to find nearly so much use in well boring as in the sister industry of oil refining, not touched on in this paper, but possibly the discussion may reveal some hidden possibilities in this direction, and, if so, the authors would give such additional information as they can.

In conclusion, the authors beg to thank the directors of Messrs. Vickers, Limited, for permission to read this paper, and again to express the hope that it may do something to further the frank collaboration between the makers and users of oil-well steels, and so increase the efficiency of both.

DISCUSSION.

The Chairman said he regarded the paper as one of the most useful which had been read before the Institution. It touched on a subject which had not been dealt with before in the proceedings. That, to his mind, was rather a strange fact, because, as the authors had pointed out, the present-day knowledge of the serviceable qualities of steel had been achieved very largely by the very costly process of trial and failure; and one knew what tremendous cost might be involved by failure in the case of a deep boring.

Those who had only had the paper put into their hands that evening would hardly be in a position to raise much discussion on many of the points which were laid down in that later section of the paper, but he did hope that several interesting questions might be put to the authors, because many of those present that evening had had experience of the costly trial-and-failure process, which had given them, perhaps, an idea that a certain type of steel was going to be the one they would select in the future, but who, when they had selected that steel, in very many cases had been surprised at the bad results which it had given.

The paper was full of interest from the point of view of the structure and mechanical properties of steel in relation to the general uses of steel in practice, but he was not quite sure that some of the people who had had large experience in drilling would agree with the authors when they said that much the same conditions of treatment and types of material which gave good results for certain mechanical things like the crank-shaft of an aeroplane engine were going quite to harmonise with what happened very often with long lengths of rods and bits and jars, and so on, in the case of wells.

One thing which he thought the members would liked to have heard a little more upon from Mr. Dickenson was in connection with his remarks on fracture. Mr. Dickenson had divided fracture into three sub-divisions—distortion, failure and fatigue—and then he had merely mentioned sudden snapping. Mr. Dickenson had not had much time to say anything very fully about sudden snapping, but some people had had unpleasant experiences of sudden snapping, and that they would very much like to know whether Mr. Dickenson could throw any light upon that point.

Mr. W. H. Fordham enquired whether there were any practical methods of testing iron and steel on the field to discover in what crystalline state they were. For instance, could a crank-shaft be tested to find out if there was a growing flaw, or could experiments be tried on a bit to find out if it had been partially burnt, or whether it was actually in the crystalline state in which it ought to be?

Mr. F. A. Ruddock said there were one or two points to which he would like to draw attention. One was with regard to sucker rods. It had been stated that rods often failed from fatigue, and on page 20 of the paper certain steels with certain mechanical properties were given. For instance, in mild steel 15 tons per sq. in. was stated as the yield point. Were engineers justified in taking the yield point as sufficient on which to base their calculations? The yield point of the steel did not express the fatigue range of the steel. For instance, a steel giving 17 tons per sq. in. yield point would probably give something of the order of 13 tons as the plus fatigue stress, and it seemed to him that if engineers were not going to experience difficulty they should take the fatigue of the metal. Taking the fatigue stress was no easy matter. It entailed time and also experience. In the Report to the Air Ministry, Material Sections, in 1921 there was a very interesting paper, in which was given a table, comparing the fatigue stress with the yield point of the material, and it was further shown that if one took a factor of ·45, and multiplied the maximum stress by it one would get approximately at any rate the fatigue stress that a material would stand up to.

He would also like to bring before the meeting some interesting specimens of drill rods which Prof. Brame had kindly passed on to him. Prof. Brame had received them from Mr. Miller, who had brought them back from the oilfield. The steel had been made in Czechoslovakia. On examination of the steel it had been found that the carbon content was about 0·25%, and the sulphur and phosphorus was about 0·1%. That was an extremely high figure. The steel had been examined under the microscope, and it had been found that the phosphorus and sulphur, which was the average phosphorus and sulphur of the rod, was concentrated into small lines running right along the rod. If engineers were going to use material like that they were bound to have trouble. Engineers could not be too careful in their choice of material for all parts liable to alternating stresses.

Mr. A. Beeby Thompson said it was very difficult for him to speak on the subject of the paper, as it dealt with a very highly specialised branch of engineering. The paper was an extremely interesting and valuable one, because it threw light upon one of

the most important problems with which the industry was now faced. Personally he was in the unfortunate position of a consultant, where on one hand he was attacked by the operators if the tools failed to give satisfaction, and on the other hand he had to satisfy the directors, who would accept no excuse if the selected material failed in practice. Oilfield equipment was very roughly used or, rather, abused in the field and manufacturers had no light task in producing materials which would withstand the treatment to which it was subjected.

In rotary drilling with high power and quick running machines drill pipe and bits were subjected to punishment which one could scarcely believe any metal capable of resisting for long. Thanks to the metallurgist and the engineer great advances are being made in producing suitable metal for specific duties.

Assisted by practical operators, British manufacturers have for some years been concerning themselves more and more in oilfield tools, and they have succeeded in capturing some of the trade formerly exclusively American. In a number of cases British tools had not given satisfaction at first, because of a lack of appreciation of the need for some particular property, but a close study of field requirements and a critical examination of defective samples had reduced the number of these errors. Operators were largely in the hands of manufacturers for the determination of the specification of metal for a particular duty. The ordinary manufacturer had little conception of the way in which tools were used in practice, as text-book conditions rarely prevailed. In practice enormous stresses were thrown on drilling plant when the holes were crooked or when boulders or hard streaks had to be passed. It was the same with sucker rods used in pumping deep wells. It was impossible to calculate the stresses one had to deal with under the varying oilfield conditions, where crooked holes and sand troubles are frequent. He was pleased to note that manufacturers were giving so much attention to the subject of producing materials to meet the ever-changing and more exacting conditions of technique met with in the oilfields.

Mr. F. G. Rappoport asked the authors what, in their opinion, was the position with regard to steel in the future. On page 23 they stated, "Any further increase in stress due to faster drilling will have to be met by the use of special heat treatment, or even the use of alloys, as it would be inadvisable to increase the carbon content beyond 0·50 per cent." Did that mean that the limit was being approached when the steel makers could not improve the material, and when it would be necessary to increase the size of the tools, and hence of the wells, and so increase the cost of drilling, and the cost of the product obtained from the wells?

Prof. W. H. Merrett said the authors had approached a very difficult subject in a very able way, and, further, they had not been afraid to specify various classes of steel for the widely different requirements of an oil-well plant. In the paper were given the chemical analyses and mechanical tests and, although there was not much said about microscopical examination, the authors had gone into the heat treatment of steels very thoroughly.

In connexion with the specification of metals for mining machinery Mr. Algernon Del Mar stated in April, 1914, in the "Mining and Engineering World" that: "it is about time for us to get into line with scientific engineers and not stay in the hit-or-miss class." In January, 1921, in a paper to the Institution of Mining and Metallurgy, Mr. E. A. Wraight pointed out that manufacturers of mining machinery seem singularly reluctant to impart any information with regard to the analyses and tests they employ. Every part of a gun, aeroplane or locomotive is carefully standardised; rails, tyres and axles are bought according to specification; but, for mining work, even such materials as drill steel, are too frequently purchased according to brand only—this means nothing, and may be a "cloak" for inferior material. It is essential that there should be careful specification and inspection of oil-well steels, especially as materials have generally to be transported long distances.

In Table II., page 14, suitable compositions for various types of bits are given, and it is interesting to note that a low percentage of manganese is specified throughout, which, together with a minimum of sulphur and phosphorus appears to be essential. The last-mentioned elements are the enemies of all engineers and, if present in appreciable percentage, are liable to cause flaking, cracking and fracture. This is also the case with dies used in metal pressing, where it has been found that the longest life and best results generally can be obtained from straight steels containing very little else than carbon.

Mr. T. G. Madgwick thought it the first publication dealing with the application of metallography to oil-well supplies. Actually we know very little about the mechanics of the underground part of well-drilling operations, and it is largely guesswork as to what the nature and amount of stresses might be to which the tools and casing were subjected. He would, therefore, like to ask if there were any possibility of the application of metallography which, by a process of working backward, could throw light upon the work actually being done by the tools in a well from a study of the strains induced thereby.

Mr. Basil Gray writes:—Considerable prominence has been given in the Press recently to experiments carried out by the

United States Bureau of Mines, using lead or salt baths for heating fishtail bits before hardening.

This process was not dealt with in the paper, and some comments on the results given by Shapiro* would seem to be not out of place.

That very accurate temperature control can be obtained is perfectly true, and if there were no disadvantages the use of lead baths would be much wider than it is at present for heat treatment in all branches of engineering.

No cheap and at the same time altogether satisfactory material has, so far, been discovered for the containing pot.

As stated, good grey cast iron is the best cheap material, but its life will be short, even when of the best quality, particularly if the heating flame be at all "cutting," and where slight blow holes occur failure will be rapid, since the flame will attack the weak spot and soon penetrate to the lead.

Numerous alloys are on the market, which will resist the action of the flame to a degree which generally varies in direct proportion to their cost, but it is recommended that either the grey iron mentioned above should be used, in which case several spares should always be kept in stock; or else one of the alloys consisting almost solely of nickel and chromium which are now made by several firms, some of which are highly successful in resisting flame attack in case-hardening furnaces where, of course, they are subjected to a much higher temperature.

These alloys are expensive, but will give a minimum of trouble.

The pots should be heavily ribbed on the outside, as the weight of the lead is sufficient to distort the pot at the temperature used, unless this precaution is taken.

It is worth noting that a lead bath cannot be used successfully for dressing on account of the much higher temperature required, so that the more usual type for furnace must still be available in addition.

Moreover, it is during the dressing operation that decarburisation of the cutting edge of the bit is most likely to occur, so that the advantages claimed for the lead bath would seem to be overrated from this point of view.

To sum up the advantages to be gained by the use of a lead bath are considerable where expert tool dressers are not available, but where they are, the gain in efficiency of the bits claimed, would appear overrated.

It is essential that the greatest care be taken in the selection of the material for the lead pots.

---

* Shapiro. The *Oil Age*, November, 1925.

Mr. Dickenson, in reply, said it was quite true, as the chairman had pointed out, that it was not always possible to harmonise the conditions which gave good results in such parts as crankshafts with those prevailing in regard to oil-well parts. However, this was only true because one could usually find out how a broken crankshaft had been used with tolerable precision—though even that was more difficult than it seemed—whereas one had much less chance of getting to know what had happened underground, as, indeed, Mr. Beeby Thompson had said. That was the most difficult aspect of the selection of steel for oil-well work—to know what had happened to a tool in service. The drillers who were handling the tool quite frequently could not ascertain exactly what happened in the hole, but much more could be done than had been usual in the past. The real purpose of the paper was to urge on those who were using tools, or other steel parts, and having failures with them, to try to find out as accurately as possible the working conditions—particularly noting any abnormalities—and to pass that information back to the steel maker, instead of simply returning tools with the complaint that they had gone wrong, and that there "must" be something faulty about the steel. If the paper contributed a little to that end it would not have been without usefulness. The application of similar methods to the selection of armament steels, aircraft steels, and automobile steels, had led to tremendous advances, because of the accurate co-ordination of service conditions and mechanical properties, made possible by the frank, and very quick exchange of views between engineers and steel makers.

Mr. Fordham asked whether there were any practical methods of discovering, on the field, the crystalline state of any particular piece of steel, or of discovering the presence of a growing flaw or burning. Burning unfortunately often disclosed its own presence by causing chipping, breaking, and so on, the fractures showing a characteristic coarsely granular condition, but for a more particular examination it is necessary to resort to the microscope. As regards the detection of growing flaws in forgings, these could be readily discovered by cleaning the forging in which a flaw was suspected, and then whitewashing it, after which the application of a bump, or a few blows with a hammer, would make a fatigue flaw, which previously could not be found at all, even by the use of a magnifying glass, become plainly visible by the appearance of a line of oil globules on the whitewashed surface.

It was an extraordinarily sensitive test, which was often used in locomotive repair shops, and could be applied to many other kinds or work. If the method were applied to drilling stems, for example, it might often be possible to avoid very expensive breakdowns in the well.

Mr. Ruddock had asked whether, as regarded sucker rods, engineers were justified in taking the yield point as a sufficient indication of the fatigue limit. In their (the authors) opinion the yield point meant very little, except in relation to one particular kind of failure; that was to say, failure by deformation under directly applied loads, when it was, of course, a physical property of the first importance. To determine the resistance to fatigue stresses it was necessary to ascertain the true elastic limit of the steel, and here it was possible to talk in a circle, and say that for resisting fatigue a high elastic limit was required, then defining the elastic limit as the same physical property as the fatigue limit.

At the present time all the Air Ministry specifications, to be used for most severely stressed steel parts where failure was quite specially disastrous, now disregarded the yield point entirely, and did not even stipulate an elastic limit, or rather, limit of proportionality, in tension. The latter value is apt to be misleading because of internal stresses in the test piece, and, altogether, it is better to depend on the determined ratio of fatigue limit to maximum stress in tension. As indicated by Mr. Ruddock a steel of any given analysis, subjected to some given heat-treatment, gives a fairly definite ratio between the fatigue limit—or the limiting range of fatigue stress—and the maximum stress in tension. Apparently, it was merely a fortuitous sort of ratio, but it was a plain fact that one could best ensure a sufficient fatigue resistance of a given piece of steel by measuring its maximum stress, other tests being applied to make sure that the correct heat-treatment had been given. For this purpose the impact test was very useful, and this might be supplemented, in special cases, by microscopic examination.

Any member who wished to go further into that matter should read, as suggested in the paper, Gough's book on "The Fatigue of Metals."

As regards the interesting case of the Czechoslovakian Steel drill rods mentioned by Mr. Ruddock, the use of such impure steel was not only highly undesirable, but quite unnecessary. Even quite cheap steel was available which had nothing like so much phosphorus and sulphur in it.

Mr. Beeby Thompson had made some observations of great interest to the authors. Undoubtedly the stresses thrown upon drilling plant are often incalculable, and sometimes the kind of information asked for in this paper is unobtainable, but clearly this makes it all the more necessary that every effort should be made to give the steel maker the fullest information possible under the circumstances. Without this it was impossible to obtain any light at all.

Mr. Rappoport wished to know what was the position with regard to the special steels of the future, and whether the limit of capacity of the present material was being approached.

He thought that engineers and designers were far from having reached the capacity of existing material to withstand stress under good conditions. Although there have been speculations regarding steels of the future, having mechanical properties far beyond those of any existing materials, it is difficult to see how any new combination of alloys can greatly improve upon those known at present. Until something very essentially new comes along, the alloy steels of to-day offer very high mechanical properties for use by the engineer, who has not yet exhausted their possibilities. In cases of severe stressing much could be done to ease the burden on the steel by lessening stress concentration, which was nearly always the cause of fatigue, and which was largely brought about by badly arranged shoulders, grooves, accidentally introduced notches, and by improper conditions of service.

He had to thank Prof. Merrett for his remarks, but had no idea that in giving specification figures he and his colleagues were showing great boldness. The specifications were really a side issue in the paper, which was intended rather to deal with first principles, but those given are proved by experience to be quite workable, and did enable the user to get material suitable for the work indicated.

Mr. Madgwick asked whether metallographic examination would determine what had happened to material by a process of working backwards. In many cases it certainly would, but this depends to a certain extent on the kind of work. Thus when an investigation of a case of failure by fatigue shows that a growing flaw has commenced at a sharp fillet or groove, there is evidence of local overstressing exceeding the capacity of the steel, and if tests show that the material was all right and up to specification, that overstressing is proved to have been excessive, and due to something in the working conditions. In some cases it is possible to blame the sharpness of the groove, but in others it is necessary to refer the matter to the engineer.

The "post-mortem" examination of forgings which have failed in service is, in fact, an important and fascinating branch of metallography, and often indicates possibilities of improvement either in the steel, or the design, or the working conditions, which will completely eliminate similar failures in the future.

On the motion of the chairman a hearty vote of thanks was accorded to the authors for their paper, and the meeting terminated.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The Ninetieth General Meeting of the Institution was held at the House of the Royal Society of Arts on Tuesday, January 12th, 1926, Sir T. H. Holland in the Chair.

The Secretary read the names of members elected since the last meeting, as follows :—

Members.—Frans A. A. van Gogh, Walter Miller and Michael Leo Steinschneider.

Associate Members.—Vladimir N. Andreev, Havelock Clive-Smith, Karl I. Luts, Percy Joseph Russell, Henry Stuart Tegner and John Lionel Wells.

Students.—Norman Macdonald Brodie and Antony F. H. Gee.

The following papers were then read :—

The Vapour Pressures of Fuel Mixtures.—Part II.

J. Stanley Lewis, B.Sc. (Wales), A.I.C.

In a paper on "The Vapour Pressures of Binary and Ternary Fuel Mixtures," read before the Institution of Petroleum Technologists (*vide Jour. Petr. Techn.*, XI., 49, 1925), a method was described briefly for determining the vapour pressures of mixtures, and reference was made to the vapour pressures of solutions of the various types of hydrocarbons. The present work is a continuation of the above, special attention being paid to the influence of alcohol, the utilisation of which in fuel mixtures is more than a theoretical possibility. The addition of alcohol to hydrocarbons gives rise to mixtures of maximum vapour pressures or minimum boiling points, and in order to make comparative tests the solutions of pure alcohol and (*a*) Hexane C_6H_{14} (paraffin); (*b*) Cyclohexane C_6H_{12} (naphthene); (*c*) Benzene C_6H_6 (aromatic) were studied.

As previously mentioned, the vapour pressure of any one of these hydrocarbons is raised by the addition of alcohol, and also the vapour pressure of alcohol is raised by the solution of the hydrocarbon until a maximum vapour pressure is reached at a particular

concentration which varies slightly with the temperature. The three possible binary solutions will be :—

i. Alcohol-Benzene.
ii. Alcohol-Cyclohexane.
iii. Alcohol-Hexane.

The first of these has been studied in the above-mentioned paper, and Table I. of the present paper contains the vapour

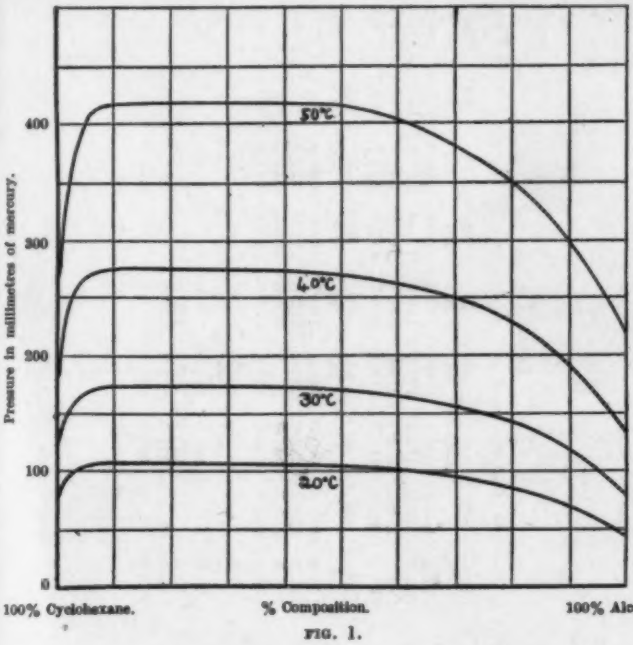


FIG. 1.

pressure determinations of alcohol with varying percentages by volume of (*a*) Cyclohexane ; (*b*) Hexane.

Vapour pressure-composition isothermals have been drawn for these mixtures, and are shown in Figs. 1 and 2. They indicate clearly the great rise in vapour pressure, and also the fact that only a very small percentage of alcohol serves to raise the vapour pressure of the mixture almost up to the maximum point. A comparison of these figures reveals that the maximum vapour pressure obtainable in any of these binary mixtures is greatest

TABLE I.

Vapour Pressures in Millimetres of Mercury of Alcohol with (a) Cyclohexane; (b) Hexane; (c) A Blend of Hexane and Heptane.

	Temp. °C.	% Cyclohexane / % Alcohol ..	100 / 0	95 / 5	90 / 10	80 / 20	70 / 30	60 / 40	50 / 50	40 / 60	30 / 70	20 / 80	10 / 90	0 / 100
(a)	20		77·7	104·1	106·2	106·5	105·8	106·8	104·0	101·5	96·6	87·0	69·8	44·2
	30		122·9	170·3	173·1	174·7	173·9	174·0	171·6	165·8	157·1	143·9	118·5	79·0
	40		183·5	268·2	273·7	275·9	274·7	274·9	270·5	263·6	249·7	229·3	193·2	133·5
	50		272·2	404·0	416·9	418·1	418·7	419·0	417·5	403·2	379·2	352·6	300·6	220·3
		% Hexane .. / % Alcohol ..	100 / 0	95 / 5	90 / 10	80 / 20	70 / 30	60 / 40	50 / 50	40 / 60	30 / 70	20 / 80	10 / 90	0 / 100
(b)	20		135·0	148·5	149·0	148·7	146·7	142·5	140·9	134·2	127·7	110·5	86·8	44·2
	30		211·5	234·2	236·8	234·8	232·8	228·0	224·3	217·2	203·0	177·5	140·7	79·0
	40		322·5	359·6	364·7	362·2	360·5	353·1	346·2	334·5	314·7	268·1	222·9	133·5
	50		478·0	530·7	539·6	537·5	535·7	528·3	517·9	500·9	475·0	422·4	343·4	220·3
		% Blend .. / % Alcohol ..	100 / 0		90 / 10	80 / 20	70 / 30		50 / 50			25 / 75		0 / 100
(c)	20		76·7		108·5	111·4	108·3		105·3			94·1		44·2
	30		123·5		175·1	179·4	176·8		171·2			152·0		79·0
	40		186·0		277·3	281·3	277·9		272·8			242·4		133·5
	50		275·2		423·0	428·7	424·5		416·5			373·2		220·3

Pressure in millimetres of mercury.

in the case of alcohol-hexane, which was to be expected from the higher starting-point vapour pressure of hexane; whilst cyclohexane has a more marked effect than benzene, although the vapour pressures at corresponding temperatures and boiling points of these two compounds are almost identical. The volatility of hexane, however, is greater than the others, and in order that a

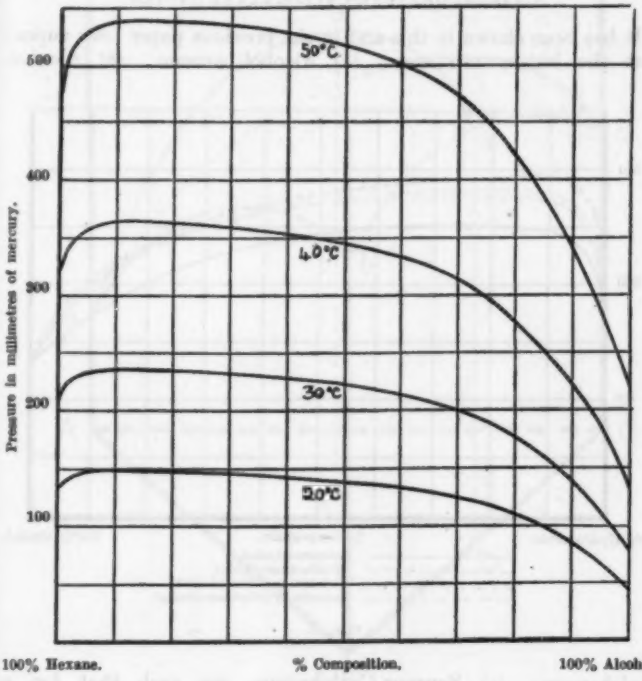


FIG. 2.

better comparison of the effect of paraffin hydrocarbons alone might be made an amount of heptane was added to hexane in such quantity as to reduce the vapour pressure of the resultant mixture to a close approximation of those of benzene and cyclohexane In Table I. (*c*) is given the determinations of the vapour pressures of this paraffin mixture with progressive additions of alcohol. The results are somewhat higher than those obtained for Alcohol-Cyclohexane mixtures which, in turn, are above those of alcohol

benzene solutions. These differences are demonstrated more clearly in Fig. 3, where the vapour pressure-isothermals of the different mixtures have been drawn for 40° C. It may be pointed out that the specific gravity of benzene is the highest, whilst the blended paraffin hydrocarbon is lighter than Cyclohexane.

Alcohol-Benzene-Cyclohexane System.

It has been shown in this and in the previous paper (*vide* supra), that the binary mixtures: (*a*) Alcohol-benzene; (*b*) Alcohol-

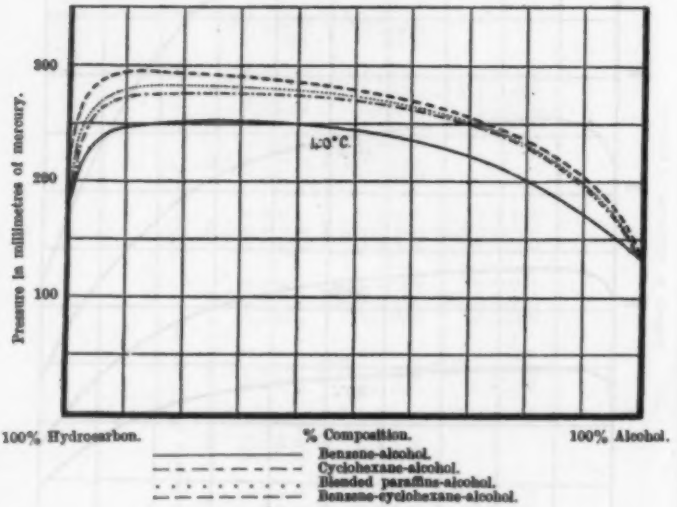


FIG. 3.

Cyclohexane; (*c*) Benzene-Cyclohexane, are such that for a particular concentration a maximum vapour pressure obtains—*i.e.*, the addition of any one of these components to any other results in a raising of the vapour pressure.

From this it follows that the addition of one of the components to a mixture of the other two will result in a homogeneous solution of still higher vapour pressure, that is to say, the ternary system is one in which a fourth and highest vapour pressure or minimum boiling point is obtained for a certain composition. This is represented diagrammatically in Fig. 4, making use of the usual

solid diagram for ternary mixtures. A, B and C are Alcohol. Benzene and Cyclohexane, which exert vapour pressures corresponding to Aa, Bb, and Cc at a temperature t° C. The curves ab, bc and ca are the isothermal-vapour pressure curves of the binary mixtures corresponding to compositions of points along A B, B C and C A. These curves have been drawn to scale in

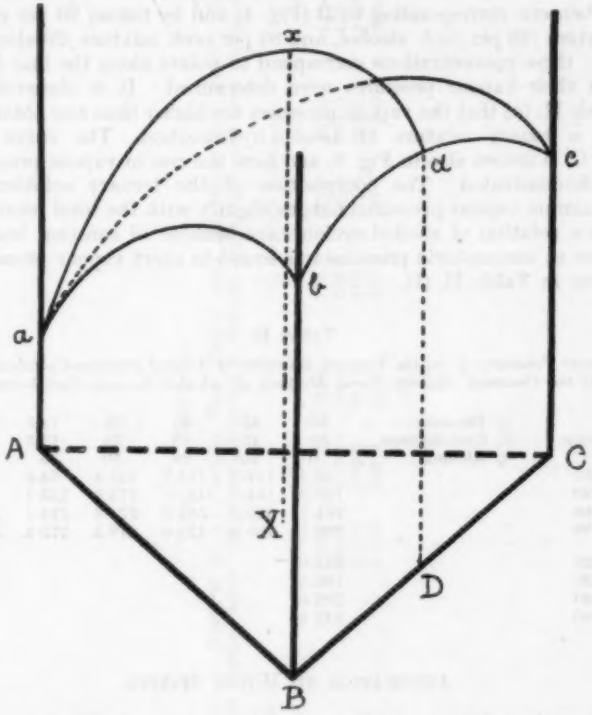


FIG. 4.

this and in the previous paper for temperatures of 20°, 30°, 40° and 50° C. A mixture of Benzene and Cyclohexane corresponding to D in the figure will have a vapour pressure represented by Dd. If, now, progressive quantities of alcohol are added to this mixture, a vapour pressure isothermal such as a x d is traced. For one particular concentration of the ternary mixture (X) a vapour pressure (say x) is obtained which is highest of all, and

this point is the summit of a domed-shaped surface. This surface is the vapour pressure surface for the ternary mixture, and for a concentration X of the ternary solution the vapour pressure is represented by the perpendicular Xx drawn to the dome surface.

To show this rise of vapour pressure for a ternary mixture experimentally, a vapour pressure curve such as a x d has been worked out by first of all preparing a mixture of 50 Cyclohexane-50 benzene corresponding to D (Fig. 4) and by taking 90 per cent. mixture /10 per cent. alcohol, and 80 per cent. mixture /20 alcohol, etc., these concentrations correspond to points along the line A D, and their vapour pressures were determined. It is observed in Table II. (*a*) that the vapour pressures are higher than any obtained for a binary mixture of alcohol-hydrocarbon. The curve for 40° C. is drawn also in Fig. 3, and here the rise in vapour pressure is demonstrated. The composition of the ternary solution of maximum vapour pressure changes slightly with the total pressure, but a solution of alcohol-cyclohexane-benzene of constant boiling point at atmospheric pressure was found to exert vapour pressures given in Table II. (*b*).

TABLE II.

Vapour Pressures of (a) the Ternary Mixtures of Alcohol Benzene-Cyclohexane; (b) the Constant Boiling Point Mixture of Alcohol-Benzene-Cyclohexane.

	% Benzene ..	50	45	40	25	12·5	0
Temp.	% Cyclohexane..	50	45	40	25	12·5	0
° C.	% Alcohol ..	0	10	20	50	75	100
(*a*) 20		86·9	114·2	112·7	107·4	94·6	44·2
30		130·2	184·7	181·2	173·2	153·1	79·0
40		201·7	290·6	284·3	274·8	244·1	133·5
50		290·1	438·9	433·0	419·5	375·8	220·3
(*b*) 20		115·0					
30		186·5					
40		292·6					
50		442·8					

APPLICATION TO MOTOR SPIRITS.

Samples of three spirits were obtained by distillation up to 120° C., and then adjusted by the addition of heavier or lighter fractions, so that the vapour pressures were almost identical. (i.) and (ii.) were obtained from paraffin and naphthene base spirits, whilst (iii.) was a motor benzole. Table III. shows the effect of adding 10, 20 and 30 per cent. alcohol to these distillates. The results are in agreement with what might be expected from the foregoing work on the pure hydrocarbons, namely, increases in the following order:—(*a*) Paraffin; (*b*) Naphthene; (*c*) Aromatic.

TABLE III.

Vapour Pressures of Alcohol in Mixtures of (i.) Paraffin Base Petrol; (ii.) Naphthene Base Petrol; (iii.) Motor Benzole. These spirits were distilled below 120° C. and adjusted so that the vapour pressures were almost identical.

Temp.	Mean Pressure of	% Alcohol added to:								
°C.	(i.), (ii.) and (iii.).	(i.) 10	20	30	(ii.) 10	20	30	(iii.) 10	20	30
20	.. 107·0 ..	128·0	133·5	132·0	126·0	129·0	127·0	117·0	119·0	118·0
30	.. 164·0 ..	205·5	210·0	208·0	202·0	205·5	204·0	190·5	192·0	191·0
40	.. 240·0 ..	316·0	326·0	325·5	310·5	321·5	320·5	285·5	288·5	287·0
50	.. 340·0 ..	472·0	489·0	490·0	465·5	483·5	483·0	428·0	444·0	444·5

Alcohol-Water-Benzene-Cyclohexane System.

The addition of water to the above-mentioned ternary system must necessarily lead to still higher vapour pressures, because the four liquids are capable of giving a quaternary maximum vapour pressure mixture. The composition of this mixture of maximum vapour pressure or minimum boiling point is such that at ordinary temperatures it separates into two phases. It is of more service as far as motor fuels are concerned, to know how much water the alcohol may contain and still produce a homogeneous mixture when blended with petrols, and this point will be discussed later.

Now if any one of the above liquids is added to another, it has been shown that the resultant vapour pressure is raised so that in all six pairs of binary maximum vapour pressure solutions can be obtained. These are :—

(*a*) Alcohol-benzene.
(*b*) Alcohol-water.
(*c*) Alcohol-cyclohexane.
(*d*) Benzene-cyclohexane.
(*e*) Benzene-water.
(*f*) Cyclohexane-water.

In the case of (*f*) the vapour pressure of all compositions will be constant at a given temperature, and will be the sum of the vapour pressures of the single components. This is comparable with the benzene-water system. All the other binary systems have been discussed previously.

The possible ternary systems from the four liquids are :—

(*a*) Alcohol-benzene-water.
(*b*) Alcohol-cyclohexane-water.
(*c*) Alcohol-benzene-cyclohexane.
(*d*) Cyclohexane-benzene-water.

These are all mixtures capable of giving ternary maximum vapour pressures or constant boiling point mixtures. Of these (*a*) has been studied fully in the previous paper for temperatures between 0°C. and 50°C., and (*c*) has been dealt with in the present paper. As regards (*d*) the cyclohexane-benzene mixture is practically insoluble in water, and the resulting heterogeneous mixture must have a vapour pressure which is the sum of the vapour pressure of water and of the hydrocarbon mixture. If these two hydrocarbons are present in such amounts that they yield a binary mixture of maximum vapour pressure, then the addition of water will produce a ternary mixture of highest vapour pressure. The

remaining system (*b*) is very similar to (*a*), which has been studies fully. The addition of one component to the other two raised the vapour pressure, but for a particular concentration the vapour pressure will be a maximum. This mixture, too, is found to be one in which heterogeneity occurs at ordinary temperatures, and if these three liquids are placed in a flask and distilled over they do so at a constant temperature at first until one of the components disappears from the mixture and the product of constant boiling point on cooling separates into two phases, even though the original solution were homogeneous. It has not been thought necessary to work out this system completely, but in Table IV. is given the variations in vapour pressure by the addition of water

TABLE IV.

Vapour Pressures of the Constant Boiling Point Mixture of Alcohol-Cyclohexane and the addition of small percentages of water.

Temp. °C.	Alcohol-Cyclohexane Mixture.	% Water added	0·5	1·0	2·0	3·0	4·0
20 ..	106·8		110·0	113·5	117·5	116·6	115·5
30 ..	174·7		178·1	181·8	188·0	187·4	186·0
40 ..	275·0		281·4	288·3	301·5	304·5	303·0
50 ..	419·0		427·5	436·0	453·0	463·0	461·5

to the mixture of alcohol-cyclohexane of constant boiling point. It was found that the amount of water that could be dissolved completely in the mixture was very small, being of the order of between 1 per cent. and 2 per cent. at 20° C. corresponding to a strength of alcohol of 95-97 per cent., but the rise of vapour pressure even by these small quantities of water is very appreciable. For a further discussion of petrol-alcohol-water mixtures see the former paper.

TABLE V.

Vapour Pressures of the Constant Boiling Point Mixture of Alcohol-Cyclohexane-Benzene and Additions of small percentages of water.

Temp. °C.	Alcohol-Cyclohexane-Benzene Mixture.	% Water added	1·0	2·0	3·0	4·0
20 ..	115·0		116·8	120·0	118·8	117·6
30 ..	186·5		191·0	195·3	194·4	192·3
40 ..	292·6		297·4	305·2	309·0	305·3
50 ..	445·8		453·1	462·7	471·5	461·5

This brings us finally to the quaternary mixture alcohol-benzene-cyclohexane-water. In this system when one component is added to a mixture of the other three the vapour pressure is raised, and for a particular concentration of the four there will be a final and

maximum vapour pressure greater than that of any binary or ternary mixture. This concentration also exists in the heterogeneous region, for if a mixture of the four liquors is distilled, the first distillate boils over at a constant temperature which is lower than that of any ternary mixture and on cooling separates into two phases. This is comparable with the preceding alcohol-water-hydrocarbon mixtures, and it will be sufficient here to take the

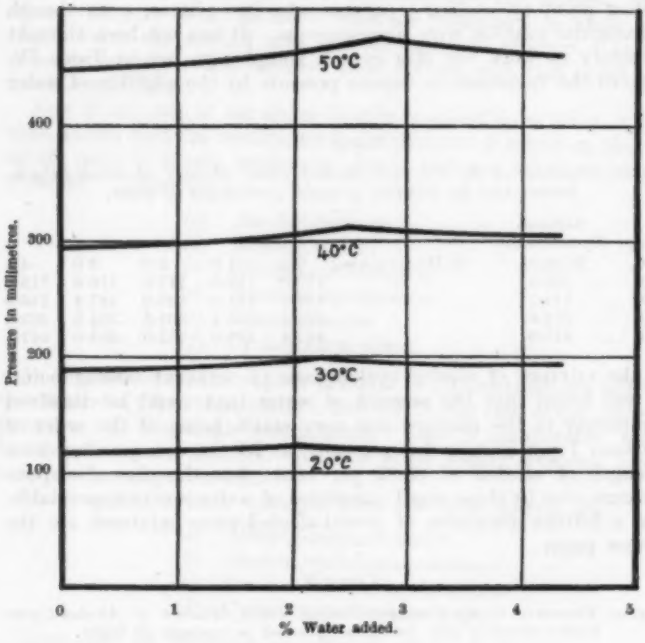


FIG. 5.

ternary minimum boiling point solution of alcohol-benzene-cyclohexane, and to show the rise of vapour pressure on addition of water. These results are given in Table V. and shown in Fig. 5. In the latter, the curves are not continuous, but show a break where the homogeneous solution becomes heterogeneous, and so these points indicate the amount of water which can be added for complete miscibility at the temperatures mentioned. The points of intersection may be joined, giving a solubility curve for water

in this alcohol-cyclohexane-benzene mixture between 20° C. and 50° C.

Thus it will be observed that the addition of water to a solution of alcohol-hydrocarbons raises the vapour pressure of the whole, but above a certain concentration of water, which is small, the system becomes heterogeneous.

The work on the above vapour pressures may be summarised as follows. It has been shown that in blending hydrocarbons only of the paraffin series, the resultant vapour pressure can be calculated approximately from the mixture formula, provided the difference in vapour pressure or boiling point of the separate liquids is not too great. In the latter case the vapour pressure of the mixture is slightly higher than the calculated, and the difference becomes more pronounced with increasing difference in the vapour pressures of the components. The raising of vapour pressures of mixtures above the calculated values is greater when a naphthene is dissolved in a paraffin and still greater with an aromatic hydrocarbon. When naphthenes and aromatics were mixed, it was found that the solution far exceeded the values calculated on the average formula, and in the case of benzene and cyclohexane a mixture of the maximum vapour pressure type is obtainable.

In the cases studied it has been found that alcohol raises the vapour pressures of all series of hydrocarbons, the effect being greatest with the paraffins and least with the benzene series. The rise is enhanced by the presence of water in the alcohol, but too great a concentration of water produces heterogeneous systems. With 98's alcohol the hydrocarbons are miscible in all proportions,

TABLE VI.

Constant Boiling Point Mixtures at 760 m.m.

Mixture.	B.-pt. °C.	% Composition			
		Alcohol.	Benzene.	Cyclo-hexane.	Water.
Alcohol-benzene	68·25	32·41	67·59	—	—
Alcohol-cyclohexane	64·75	32·20	—	67·80	—
Alcohol-water	78·15	95·57	—	—	4·43
Benzene-cyclohexane	77·80	—	32·3	67·7	—
*Benzene-water	69·25	—	91·17	—	8·83
*Cyclohexane-water	69·30	—	—	91·78	8·22
*Alcohol-benzene-water	64·85	18·5	74·1	—	7·4
*Alcohol-cyclohexane-water	62·40	20·4	—	73·8	5·8
Alcohol-benzene-cyclohexane	62·25	33·5	29·5	37·0	—
*Cyclohexane-benzene-water	67·80	—	29·6	63·0	7·4
*Alcohol-benzene-cyclohexane-water	61·95	19·8	23·1	52·1	5·0

but with 95's alcohol, complete solubility at ordinary temperatures is attained only when the proportion of alcohol present is relatively large (see former paper), and as the water proportion increases so does the amount of alcohol necessary for producing a homogeneous solution. It will be the aim of a future paper to correlate these variations in vapour pressures of mixtures with the changes in volumes and specific gravities.

In conclusion, a table is appended (Table VI.) giving the boiling points and compositions of all the possible minimum boiling point solutions—binary, ternary and quaternary. The results for alcohol, water and benzene were determined by Young (J.C.S., **81**, 710, 1902). It will be seen that the boiling points are lowered as the number of components is raised, until finally the quaternary mixture is reached with the lowest boiling point of all. This is an example of a rarely recorded mixture, namely, a quaternary mixture of constant boiling point. The distillates marked with an asterisk are not completely miscible at room temperatures but separate into two phases.

Once more the author wishes to extend his thanks to Prof. J. S. S. Brame for his continued interest and supervision of the work and for his suggestions for the furtherance of the work.

The President, on behalf of the Institution, conveyed the members' thanks to Mr. Stanley Lewis.

DISCUSSION

Mr. E. C. Craven said he would like to make one or two small suggestions. It was a matter of considerable difficulty to obtain hydrocarbons of a respectable degree of purity. Some samples of reputed normal paraffins recently examined by Dr. Ormandy and himself had shown a purity of round about 40 per cent. He would point out, therefore, that in a paper like Mr. Lewis's giving valuable data relating to mixtures of pure bodies, sufficient figures should be given to enable an estimate to be made of the purity of the bodies employed. In the case of benzene and cyclohexane the melting points were sufficient. In other cases the density and refractive index were probably the most useful data to give.

He was under the impression on first reading over both parts of the work that the compositions were given by volume, but later it seemed more probable that they were by weight. In that connection the question of the mixture formula which the author had employed was open to question. Where normal liquids of the same type were mixed, there was no doubt that reasonably accurate

calculations of the vapour pressure of the mixture could be made, using Speyer's formula, namely,

$$\text{Vapour pressure of mixture} = \frac{\Sigma\, n\, p}{\Sigma n}$$

where n = No. of molecules of a component and p its vapour pressure.

As pointed out by Young in his new edition, page 29, Guthrie was clearly in error in taking percentages by weight. As he (Mr. Craven) had already said, molecular percentages should be employed. If the author's previous figures on mixtures of petrol fractions of a paraffin type be examined, they would confirm that statement, since the weight mixture formula exaggerated the effect of the heavier fractions and gave too low calculated vapour pressures.

With regard to benzene and normal hexane, Young said that a binary mixture of minimum boiling-point was formed. The author's figures did not confirm that, and it illustrated the difficulty there very often was in arriving at definite results concerning azeotropic mixtures. In the case of alcohol-water mixtures Young himself found that by distillation the true binary mixture containing 4·4 per cent. weight of water was never obtained, but mixtures containing 7·6—8·0 per cent. weight.

In dealing with the ternary mixture alcohol-benzene-cyclohexane, since each pair formed a binary mixture of minimum boiling-point, the author said it followed that all three together would give a ternary mixture of minimum boiling-point. While that was no doubt very probable, personally he did not see that it followed at all. The difficulty of determining the existence and composition of even binary mixtures made it advisable that a little more information should have been given as to how the compositions of the ternary mixtures were arrived at, and also of the quarternary mixture. The binary mixtures, alcohol-cyclohexane, benzene-cyclohexane, and the ternary mixture alcohol-cyclohexane-water had been investigated by Lecat, who gave figures differing somewhat from those given in the present paper.

In conclusion, it might be worth pointing out that for mixtures of hydrocarbons, if the boiling-point T_B be known the vapour pressure could be fairly accurately calculated for the other temperatures, since the relation between log p and T_T^B was practically linear, and the same for all hydrocarbons. From the practical standpoint the low boiling-point ternary mixture was of interest, since a spirit which had just been examined by Dr. Ormandy and himself was very rich in aromatic and naphthenic constituents, and it was

obvious from the work done by Mr. Lewis that addition of commercial alcohol to that spirit would produce a fuel of a very volatile and valuable character.

Dr. A. E. Dunstan said he desired to raise a question of terminology. What did the author mean by "vapour tension" and by "vapour pressure"? Personally he thought the term "vapour tension" should be reserved for homogeneous mixtures of pure liquids, and that "vapour pressure" should be reserved for those heterogeneous mixtures which were dealt with in the industry. For example, one might get a sample of oil from the well containing gas, water, and petroleum hydrocarbons. The observed vapour pressure in that case was quite a different thing from the actual vapour tension known to the physicist.

Mr. J. Stanley Lewis, replying to Mr. Craven, said that the only vital point that he had raised was the purity of the substances. One of the drawbacks of the static method of determining vapour pressures was the questionable purity of the liquids, and so, every precaution was taken to obtain individual liquids of as high a degree of purity as possible, and which gave finally vapour pressure results that were in close agreement with those of Young and Regnault. The physical data mentioned by Mr. Craven were assuredly of great importance, but would necessitate extreme care and accuracy to reveal, for example, the presence of 0·05 per cent. of water in benzene, an amount which produces an appreciable error in the vapour pressure. And so, though physical data such as boiling-points and densities were taken into consideration, no liquid was employed which did not conform to the vapour pressure test. The sample of hexane was one which had been specially prepared for him, and might be said with safety to possess a purity higher than 40 per cent. Judging by the varied physical data published for hexane, it was doubtful whether anyone had obtained a really pure sample of this hydrocarbon.

The compositions of the solutions were expressed in volumes throughout, and this would not affect the simple mixture formula given in the former paper. It was only in the case of liquids which had no effect upon each other that the mixture formula would be "obeyed." The isothermal for a binary mixture would then be a straight line joining the vapour pressures of the components and this would hold good, even though the compositions were expressed in volumes, weights or molecules. It was the object of the author to show the extent to which the actual vapour pressure—isothermals deviated from the simple mixture formula, or straight line graph. Furthermore, the maximum vapour pressure attained in a given mixture of two or more components for a specified temperature

would be independent of the mode of expressing the composition, Thus a vapour pressure of *p.m.m.s.* would still remain *p.m.m.s.*, though the composition might be expressed as x per cent. by volume = y per cent. by weight = z per cent. by molecules. The simple mixture formula was not to be confused with those formulæ which were attempts to calculate even the approximate vapour pressures from the *molecular* percentages, nor had the author attempted a mathematical expression of the curves for the binary mixtures. In no way would the general conclusions of the paper be changed by expressing the compositions in molecular percentages.

With regard to the question of the hexane and benzene mixture he doubted if Young had stated definitely that a constant boiling-point mixture obtained, but that it was very probable. Personally, he thought that it would be a good plan to test this point by determining the boiling-point of the ternary mixture alochol-benzene-hexane, which might yield a minimum constant boiling-point mixture and at a temperature below that of any one of the binary mixtures selected from this trio. This would then suggest that the hexane-benzene mixture produced a minimum boiling-point mixture.

The author did not wish to put forward as a "law" that if three liquids were such that any pair produced a binary mixture of minimum boiling-point then the ternary mixture would yield a still lower minimum boiling-point mixture. He had tried to illustrate what happened in the solid diagram and pointed out an analogy in the eutectic points of metal mixtures. The experimental evidence was in favour of the above view, and so far he was unable to find any exceptions. Finally he realised the difficulty of determining the composition of binary and ternary mixtures, especially hydrocarbon mixtures, and the results given were the mean of various methods to be found in the literature. There was no need to recapitulate these, which would serve only to extend unduly the paper on vapour pressures, whereas the important point was the evidence for the quaternary mixture of minimum boiling-point or maximum vapour pressure. It might be reiterated that the composition of the binary, etc. mixtures of constant boiling-point varied with the pressure at which they were distilled.

With regard to the question asked by Dr. Dunstan, he would not care to enter into a controversial matter of that kind. Apparently, the terms "vapour tension" and "vapour pressure" are used indiscriminately, but there were some who advocated the former for the liquid and the latter term for the vapour itself. (Compare Ostwald's "solution tension" of the solid and "solution or osmotic pressure" of the dissolved substance.)

Symposium on the Estimation of Unsaturated Hydrocarbons.

Prof. J. S. S. Brame said the reason why he had suggested to the Secretary that the members might have a discussion that evening on the above subject was because so recently as two meetings ago Dr. W. R. Ormandy and Mr. E. C. Craven had read a paper on the question and had put forward certain suggestions, and he did not think that that paper had received the adequate discussion it had merited. He had thought, therefore, that the present would be a good opportunity further to discuss the matter.

The estimation of unsaturated hydrocarbons in cracked spirits was a matter of considerable importance at the present time, when large quantities of such spirit were manufactured and marketed, usually as a blend with straight gasoline. Further, the importance of aromatic hydrocarbons in gasoline was well recognised, and a method of estimation in cracked spirit was very much to be desired.

It was generally recognised that so far there were no really satisfactory methods of estimating either of those classes of hydrocarbons, especially where they occurred together. In the Institution's Standard Methods of Testing Petroleum Products, it was not found possible to include a reliable method for unsaturateds, and a special note was made that the adopted aniline point method for aromatics was not applicable "to gasoline containing an appreciable amount of olefine hydrocarbons." It might have been more broadly stated as "unsaturated" hydrocarbons.

The two principal methods suggested for estimating the unsaturated were iodine (or bromine) absorption, and treatment with sulphuric acid of suitable strength. With regard in the first place to iodine (or bromine) absorption, a great deal of work had been carried out on this class of method, two notable papers being those of Faragher, Gruse and Garner (J. Ind. and Eng. Chem., 1921, 13, 1044), and by E. M. Johansen (*loc. cit.*, 1922, 14, 288). The following objections might be urged against such methods. In the first place, it might be said that considerable differences were recorded on the question of substitution occurring, which would largely vitiate results. According to Faragher, Gruse and Garner, who carried out very complete tests with pure or nearly pure hydrocarbons with all olefines, including straight, branched chain and cyclic compounds, containing secondary and tertiary hydrogen atoms, the substitution was practically negligible. Again, later the statement occurred that with Hanus' solution (molecular pro-

portions of iodine and bromine in glacial acetic acid) the action with length of time or with large excess of reagent "in no case gave values higher than those calculated for the structure of the compounds in question," and they deduced that "Hanus' solution did not cause substitution in any of the classes of hydrocarbons dealt with," and gave results with olefines which indicated the true unsaturatedness.

On the other hand, Johansen, using carbon tetrachloride solutions of iodine and bromine of the same concentration as in the Hanus' and Wij's solutions, estimated the absorption and substitution (free acid liberated) with many samples of mineral oil products. Four results might be quoted :—

	Absn.	Subn.	A plus 2 S	Total (Hanus)
Straight lamp oil	2·4	3·7	9·8	9·26
Cracked lamp oil	8·69	9·26	27·2	26·35
Uncracked gas oil	5·36	12·32	30·0	25·71
Cracked gas oil	8·30	13·26	34·8	30·26

The author claimed those results showed that the "total iodine absorption values by Hanus' and other methods are unsuitable as an indication of the comparative unsaturatedness of petroleum products."

Secondly, the degree of absorption by hydrocarbons of different series (olefines, diolefines, alkines) was by no means determined. Faragher, Gruse and Garner found that when the iodine quantity present was plotted against weight of hydrocarbon a very steep curve was obtained for diolefines, but the theoretical maximum value for iodine absorption was never reached. Thus the maximum obtained for isoprene was 425, against a theoretical figure of 741, and for hexadiene 425 against the theoretical figure of 630. It was concluded that one double bond was much more readily attacked than the other. For the hydrocarbon heptine, with triple (acetylenic) bond the maximum value was 243, against a theoretical value of 536. In cracked spirits where there would be considerable variation in the olefine/diolefine ratios, it was difficult to see how iodine values could be a satisfactory measure of unsaturatedness.

Thirdly, iodine values were usually only relative. To measure quantitatively unsaturatedness, molecular weights would have to be known. In such a mixture as a cracked gasoline a mean molecular weight was difficult to determine with even approximate accuracy, and even so it would not appear that the effect on the mean molecular weight of the non-reactive hydrocarbons forming the bulk of any cracked spirit would be negligible. Surely what would really be required would be the mean molecular weight of the reactive (i.e., unsaturated) portion, the determination of which offered insuperable difficulties.

Fourthly, from a practical point of view the use of very small quantities of highly-unsaturated spirits for the determination might lead to inaccuracy, accurate weighing of small quantities of cracked spirits which usually had very volatile lower fractions presenting some difficulty.

Turning next to the sulphuric acid removal of unsaturated hydrocarbons, that method was condemned in no unsparing words by Faragher, Gruse and Garner, who said that it was practically useless, "since sulphonation, polymerisation, solution and possible oxidation occur along with the absorption of unsaturated hydrocarbons." Yet in the United States the diminution of volume by treatment of spirit with twice its volume of 93·2 per cent. sulphuric acid was an officially recognised test. It was, however, certain that mere diminution of volume by the use of sulphuric acid of any active strength was not sufficient, for it was well known that much of the product of reaction of the acid remained in solution in the spirit itself, raising its specific gravity, and raising its final boiling point by perhaps well over 100° C.

In this country 80 per cent. sulphuric acid was commonly employed for dissolving and polymerising unsaturated hydrocarbons. For such actions it would appear desirable to use the strongest acid which would be without action on any aromatic hydrocarbons. Experiments had been made in his laboratory, and it had been demonstrated conclusively that the American 93·2 per cent. sulphuric acid would completely remove toluene purposely added to an aromatic free petrol, the original aniline point of the latter being completely restored. Loss by the action of acid of this strength would clearly give too high a result for unsaturateds.

It occurred to him that the most suitable strength of acid for attacking unsaturateds would probably be found with the monohydrate $H_2SO_4.H_2O$, containing 84·5 per cent. of sulphuric acid. It had the advantage of easy preparation of very definite strength, since by cooling an acid-water mixture of approximately the correct strength, crystals of the hydrate, of melting point about 7° C., were obtained. Acid of that strength did not raise the aniline point of mixtures of toluene or xylenes with an aromatic free petrol (using the customary two volumes of acid to one volume of spirit). It had not been proved that an acid containing more than 84·5 per cent. and less than 93·2 per cent. sulphuric acid would attack aromatics, but with at least one cracked spirit experiments had demonstrated that after treatment with 80 per cent. acid, further treatment with 84·5 per cent. acid caused further diminution in volume, and a further rise in the aniline point.

The spirit used had a F.B.P. of 195° C., and 100 cc. were treated

with 200 cc. of different strengths of acid in succession, with the following results :—

Acid strength %	Total loss.	Specific gravity.	Aniline point.
Original	—	0·748	44·6
80	11	0·758	51·5
84·5	15	0·765	54·8
93·2	26·5	0·761	60·7
98·0	38	0·747	66·6

With another cracked spirit (F.B.P. 160°) and separately treating 10 cc. of spirit with 20 cc. of acid of the four strengths, according to the American procedure in a Babcock bottle, the following results were obtained :—

	80%	84·5%	93·2%	98%
Loss in Volume—%	9	10·5	15·5	20·5
Aniline point	46°·4	49°·1	53°·8	57°

It would appear, therefore, that 80 per cent. acid did not bring about the maximum solution, polymerisation, etc. Further experiments might prove that the definite hydrate (84·5 per cent.) did not do so, but it did completely remove amylene from a mixture made with aromatic free petrol, and so far his own experiments suggested that it was the most effective and convenient strength of acid to employ.

In a recent paper before the Institution, published in the Journal for 1925, Ormandy and Craven put forward three suggestions for the determination of unsaturated hydrocarbons : (a) loss to 80 per cent. sulphuric acid, plus the gum residue ; (b) total loss to 98 per cent. sulphuric acid less the aromatic hydrocarbon content ; (c) the amount of distillate collected within the original boiling range after treatment with 80 per cent. sulphuric acid. The latter method was merely suggested, and no results were given by the authors.

The formation of polymers soluble in the spirit by the action of sulphuric acid had already been mentioned. For the determination of aromatic hydrocarbons in cracked spirits by the aniline-point method, as required in the second method suggested by Ormandy and Craven, it must be shown that those soluble polymers did not interfere with the aniline point. That appeared to be assumed by the authors in question, but an extensive series of experiments made in his own laboratory by Mr. H. W. Pilcher did not confirm this assumption. A sample of cracked spirit was carefully fractionated and treated with (a) 80 per cent., and (b) 93·2 per cent. sulphuric acid, the distillation range and aniline points being determined. The results were as follows :—

	Original cracked spirit.	After acid treatment 80 per cent.	93·2%
Specific gravity	0·748	0·739	0·753
Distillation (I.P.T.)—			
I.B.P.	37°	39°	36°
F.B.P.	192°	255°·5 over	300°
Loss by acid	—	8%	24%
Aniline point	42°·5	49°·8	61°·5

Distillation of the separated spirit after the respective acid treatments yielded :—

		From 80 per cent. acid.	From 93·2 per cent. acid.
Boiling below 192°	Per cent. ..	90	82
	Aniline point ..	57°·4	63°·4
Boiling above 192°	Per cent. ..	8	13·25*
	Aniline point ..	46°·2	59°·5

* 3 per cent. residue in flask.

It was of interest to tabulate the aniline points for this cracked spirit after the acid treatments, and after complete sulphonation, as laid down in the standard method for determination of aromatic hydrocarbons :—

Aniline Points.

	Before removal of aromatics.	After removal of aromatics with 98% H_2SO_4.	Rise of aniline point.
Original spirit	42°·5	64°·4	21°·9
After 80% H_2SO_4—			
Whole spirit	49°·8	64°·7	14°·9
Fraction to 192°	57°·4	64°·0	6°·6
After 93% H_2SO_4—			
Whole spirit	61°·5	64°·0	2°·45
Fraction to 192°	63°·4	63°·8	0°·4

It was clear that the polymerised products in solution could not be neglected. Their effect is to lower the aniline point, and this was confirmed by further experiments in which high-boiling polymerised fractions were added to aromatic free petrol (aniline point, 58°), and to the same petrol to which a known weight of toluene had been added :—

To aromatic free— petrol added.	Aniline points. Original mixture.	After 98% H_2SO_4	Rise.	Toluene (By weight).
(*a*) 10% high-boiling polymers ..	55°·4	—	—	—
(*b*) 11·6% toluene	47°·7	57°·2	9°·5	11·4
(*c*) 11·6% toluene to mixture (*a*)	46°·0	56°·8	10°·8	12·96

There remained for consideration the other two suggested methods : (a) loss to acid plus gum residue ; (c) the distillate collected within the original boiling range after acid treatment.

A commercial cracked spirit was fractionated with a column to give a final boiling point of 160°, and was treated with 84·5 per cent. acid, the reduction of volume noted, a gum test made on a part of the washed spirit, the remainder being carefully fractionated through the same column to the same F.B.P. The results may be summarised :—

	Sp. gr.	Volume recovered.	Aniline point.	Gum test.
Original	0·753	—	41°·7	—
After 84·5% acid	0·770	92%	49°·5	1·81%
Distillation after acid—				
(*a*) to 160°	0·749	73%	51°·9*	nil.
(*b*) above 160°	0·854	18%	42°·4	—

*Aniline point after 98% H_2SO_4 was 57°·2.

The unsaturateds by method (a) would therefore be 8 (loss to acid) + 1·81 (gum) = 9·81 per cent. (approximately, since the gum is by weight), and by method (c) 100 — 73 = 27 per cent.

It could hardly be contended that when a good column was used the distillate coming over above the original final boiling point could contain more than small quantities of unaltered spirit, that is, it must be practically all polymerised material.

On the other hand, the gum residue represented only a fraction of these high-boiling polymers. In the above case actually about 70 per cent. by weight of the high-boiling fraction was lost by evaporation in making the gum test on this fraction.

It is tentatively submitted that the evidence is strongly in favour of the unsaturateds being determined by treatment with 84·5 per cent. acid until the aniline point is no longer affected, and distilling with a column to the original final boiling point, and that in this distillate the unsaturateds remaining (if any) will have no appreciable effect on the determination of the aromatics by the usual aniline point method.

There is, however, the possibility that in the distillate after the acid treatment there may be low-boiling products from the action of the acid, which were not present before the acid treatment. It is a point requiring investigation.

Dr. A. E. Dunstan remarked that at the last meeting, when the matter had come up for discussion he had put forward tentatively the suggestion that by cutting the material at the original final boiling-point or thereabouts and polymerising olefines and subsequently distilling to the original F.B.P. something in the nature of a solution of the problem might perhaps be arrived at, and for some long time past in his own laboratory that particular method had been experimented with as time had permitted. There was one point, however, which had emerged recently in connection with the strength of the

acid. If one carried out this particular operation—that was to say, polymerising the unsaturateds, and, after the operation, cutting at the final boiling-point, and if that were done with a variety of strengths of acids and the absorption was plotted against the percentage strength of the sulphuric acid, a curve showing a maximum polymerisation was obtained. The maximum absorption, presumably corresponding with the maximum polymerising, appeared at 91 per cent. strength, H_2SO_4. Possibly Prof. Brame would be able at some later date either to confirm or disprove that statement. Evidently there was some work still wanted to be done on the optimum concentration of the acid.

The next point was that he was not entirely convinced that they were dealing with unsaturateds, for the following reason: 3- or 4-membered cyclo paraffins were presumably attacked by sulphuric acid and by Wij's reagent, but not by hydrogenation. He had found in higher boiling compounds in petroleum that abnormal iodine values, solubility in acid, and inability towards reduction occurred *pari passu*.

Prof. Brame asked if that was the rate of absorption, or quantity absorbed.

Dr. Dunstan replied it was quantity absorbed.

Prof. Brame enquired on what type of spirit.

Dr. Dunstan replied an ordinary cracked spirit. That had been checked on a mixture of olefines and aromatic free petrols. It had always been assumed, rightly or wrongly, that those cracked spirits did contain olefines, paraffins and aromatics, but obviously that was only an assumption. Some years ago, working higher up in the boiling range, almost in the lubricating oil range, he had found this curious thing: if one took the ordinary Wij's iodine value, plotting time against the iodine value, the curve went up, and if the iodine value was plotted against concentration of iodine, again the curve went up; but those compounds which gave those increasing iodine values, presumably due to the absorption of iodine, were absolutely unaffected by hydrogen over a nickel catalyst. If the ordinary iodine value given by a fatty acid was compared, a perfect quantitative figure could be obtained, and it was known, further, that those fatty acids with nickel and hydrogen were easily reducible. He had been perturbed at the fact that a normal iodine value had not been obtained, and, secondly, that one could not get any catalytic reduction. He remembered at the time discussing the matter with Prof Thorpe, and it was agreed that it by no means followed that those substances giving abnormal iodine values were olefines at all. They had come to the conclusion

that there was this possibility of compounds being present in cracked spirit, entirely non-reducible but obviously capable of adding on iodine. He wanted the members to realise that they might be a little bit astray in assuming all the time that they had got ordinary olefinic bodies present.

Messrs. **E. Lawson Lomax** and **E. S. Pemberton.** In view of the fact that the production of cracked spirit is increasing largely, and is liable to become as important a product as the natural spirits, and those obtained from casing-head gasoline, it is necessary that the question of the determination of the above hydrocarbons should be investigated with a view to obtaining a standard test which can be applied possibly to all classes of motor spirit.

The present methods in use for the determination of these, while to a certain extent satisfactorily when used with straight run spirits or spirits made from casing-head gasoline, were on investigation found to be totally unsuitable when used in connection with a cracked spirit, either the modern cracked spirits produced by special pressure processes or those produced by processes working at lower pressures or at atmospheric pressures. These latter class of spirits give abnormal results with standard tests, which results are no indication whatever of the constitution of the spirit. It was therefore decided that this problem should be investigated with a view, if possible, to the development of satisfactory tests for this purpose.

The Tizard and Marshall or Aniline Point method for the determination of aromatic hydrocarbons in hydrocarbon mixtures (J.S.C.I., 1921, 207) is stated by these authors to be inapplicable to mixtures containing appreciable quantities of olefines, it follows therefore, that before this method can be applied to cracked benzines, the olefinic hydrocarbons must be removed. As will be seen from the following table :—

n — Pentane	..	..	..	Aniline Point	72° C.
n — Hexane	..	..	..	„	„	69° C.
n — Heptane	..	..	..	„	„	70° C.
n — Octane	..	..	..	„	„	72° C.
Cyclo hexane	..	..	..	„	„	31° C.
Amylene	..	..	..	..	„	„	14·5° C.

these hydrocarbons have lower aniline points than the paraffins and cyclo-paraffins, consequently their presence will lower the aniline point of any hydrocarbon mixture, whilst their subsequent removal together with aromatic hydrocarbons will have the opposite effect, resulting in an exaltation of the aromatic hydrocarbon content.

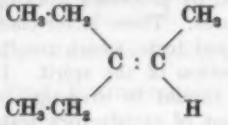
It has been widely accepted that acid of 80 per cent. concentration removes olefinic hydrocarbons, but Brooks and Humphrey (J.A.C.S., 1918, p. 882) have shown that sulphuric acid of concentrations of this order causes changes other than esterification, which itself would result in complete removal of the olefines in the acid layer. Their conclusions, which are based upon considerable experimental evidence gained by the treatment of olefines, ranging from the pentenes up to the duodecenes, with sulphuric acid of various strengths, but chiefly of 85 per cent. strength, are that the principal actions of sulphuric acid on olefines are :—

(1) Polymerisation.

(2) The formation of secondary and tertiary alcohols.

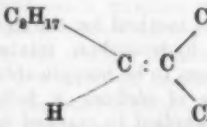
(3) The formation of mono and dialkyl esters.

Michael and Brunel (J.A.C.S., 1909, 118) had previously stated that the tendency to form alcohols and esters decreases with increasing molecular weight, these reactions being at a maximum for pentenes and hexenes. On the other hand, with increasing molecular weight polymerisation is the chief result. thus :



yields 72% alcohol and 12% polymers.

whereas



$\alpha\alpha$-dimethyl β-octyl ethene.

yields 97% polymers and only a trace of alcohol.

From the work of Brooks and Humphrey it appears that the transition from the alcohol forming olefines to the polymer-forming olefines occurs with the heptenes, e.g., iso. α-heptene (B.P. 85°—86° C.) with 85 per cent. acid yields chiefly its dipolymer whereas γ heptene (B.P. 93°—95° C.) gives no polymers, but only esters and alcohol. The octenes and higher homologues give little or no alcohols but chiefly polymers, whilst duodecene yields its dipolymer almost quantitatively.

The alcohols which are formed from the lower olefines pass into the acid layer and are eliminated, whereas the esters and polymers chiefly pass into the oily layer in which they are soluble.

The polymers which are formed are chiefly the dipolymers, and these still contain one double bond. This ethylenic linkage is more stable to sulphuric acid than is that of the parent olefines.

In order to ascertain the effect of 80 per cent. sulphuric acid treatment upon cracked spirit, a benzine of the following properties :

S.G. @ 15·5° C.	07·38

Distillation Test.

I.B.P.	29° C.
To 100° C. %	32·0
100°—150° C. %	45·0
150°—200° C. %	21·0
F.B.P.	190° C.

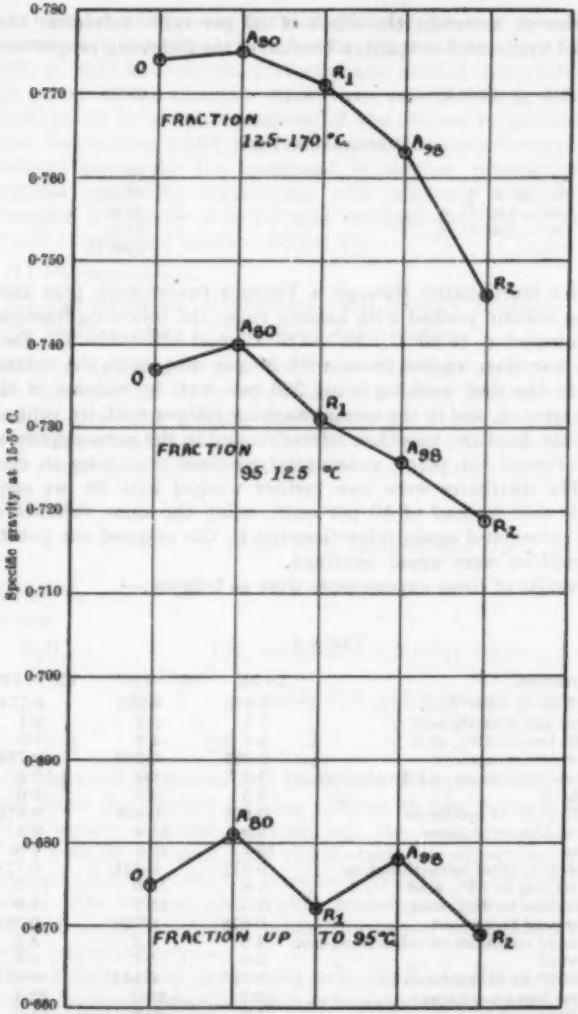
was thrice fractionated through a Young's twelve-bulb pear fractionating column packed with Lessing rings, the following fractions being collected up to 95° C.: 95°—125° C., and 125°—170° C. Each fraction was then washed twice with 80 per cent. acid, the volume of acid in the first washing being 300 per cent. by volume of the fraction treated, and in the second washing 100 per cent. by volume. Each of the fractions was then refractionated in the same apparatus to the original cut point, substantial residues remaining in each case. The distillates were now further washed with 98 per cent. sulphuric acid instead of 80 per cent., using the same volumes of acid as before and again refractionated to the original cut points, when residues were again obtained.

The results of these experiments were as follows :—

Table I.

Fraction.	To 95°	95°—125°	125°—170°
Original S.G. @ 15·5° C.	0·675	0·737	0·774
% Volume loss to 80% acid	7·7	5·2	2·1
% Weight loss to 80% acid	6·8	4·8	1·9
S.G. after acid treatment	0·681	0·740	0·775
% Volume of residuum on refractionation	7·2	6·4	2·2
% Weight of " " "	8·5	7·6	2·6
S.G. @ 15·5° C. of residuum	0·808	0·838	0·871
% Volume loss on process	14·9	11·6	4·3
% Weight " " "	15·3	12·4	4·5
S.G. @ 15·5° C. after refractionation ..	0·672	0·731	0·771
% Volume loss to 98% acid	7·8	15·5	17·2
% Weight loss to 98% acid	7·1	15·8	17·9
S.G. after acid treatment	0·678	0·726	0·763
% Volume of residuum on refractiona-tion	4·9	4·5	5·2
% Weight of " " "	5·9	5·1	6·8
S.G. @ 15·5° C. of residuum	0·795	0·841	0·878
% Volume loss on process	12·7	20·0	22·4
% Weight " " "	13·0	20·9	24·7
S.G. @ 15.5° C. after refractionation ..	0·668	0·719	0·746

The graph shows the changes in the specific gravities of the fractions as a result of the various treatments.



O Original specific gravity.
A_{80} Specific gravity after 80% H_2SO_4.
R_1 Specific gravity after distillation to original cut point.
A_{98} Specific gravity after 98% H_2SO_4.
R_2 Specific gravity after distillation to original cut point.

TREATMENT OF CRACKED BENZINE FRACTIONS WITH SULPHURIC ACID. CHANGES IN SPECIFIC GRAVITY.

The distillation ranges of the residues from the fractions were :—

TABLE II.

Fraction.		To 95° C.	95°—125° C.	125°–170°C.
After 80% acid. I.B.P. ..	° C.	90° C.	120° C.	
to 150° C.	%	10·0	28·0	
150°—200° C. ..	%	40·0	5·0	(Too small
200°—250° C. ..	%	35·0	37·0	for dis-
250°— to F.B.P. ..	%	5·0	26·0	tillation
F.P.B.	° C.	275*	283	test.)

* SO_2 evolved at 230° C., vigorous decomposition at 275° C., distillation discontinued.

After 98% acid. I.B.P.	° C.	80	120	168
To 150° C.		12·5	6·5	—
150°—200° C.		30·5	7·5	4·0
200°—250° C.		27·0	19·5	7·0
250°—300° C. ..		14·0	44·5	56·0
300°—F.B.P.		12·0	18·0	29·0
F.B.P.	° C.	314	315	345

No decomposition, as evidenced by the evolution of SO_2, was noticed in the distillation of any of the residues with the exception of the one noted.

From Table I. it will be seen that as a result of the treatment with 80 per cent. acid appreciable quantities of compounds boiling at temperatures outside the original boiling point range of the fractions are produced. It is concluded that these are almost entirely polymers, since only in the case of the fraction boiling up to 95° C. was there any evidence of the present of esters as indicated by the evolution of SO_2 on distillation. Thus it may be taken that the combined losses due to acid treatment and refractionation are attributable to olefines. Assuming this, it will be seen that only from 50—60 per cent. of this loss occurs as a result of solution in the 80 per cent. acid. It follows therefore, that unless fractionation is resorted to, a considerable amount of the original olefines remain in solution as polymers in the washed oil and, as Brooks and Humphrey have shown, these polymers are olefines.

From Table II., which shows the ranges of these polymers, it will be seen that if a benzine is treated with 80 per cent. acid as a whole and refractionated it is impossible to eliminate all the polymers, since many of them derived from the lighter fractions boil within the range of the higher fractions. As the result of fractional treatment a greater elimination is obtained than when treatment as a whole is given.

From the fact that further residues are obtained on treatment with 98 per cent. acid followed by refractionation, and that none of

these distilled with decomposition, it is concluded that further olefine polymers are produced as a result of the use of the stronger acid. Whether these are produced as a result of the presence of original olefines which are unattacked by the 80 per cent. acid, or whether polymers still remain after refractionation, which being stable to 80 per cent. acid, are attacked by 98 per cent. it is difficult to say. It was found, however, that the residues from the 80 per cent acid treatment when treated with 98 per cent. acid lost about 50 per cent. by volume due to solution, but it seems improbable that appreciable quantities of polymers remain in solution after refractionation, since the specific gravity is lower then than before treatment with 80 per cent. acid.

From the graph it will be seen that in the case of the first fraction the decrease in specific gravity due to the removal of aromatics is outbalanced by the increase due to polymerisation resulting in an increase in specific gravity after treating with 98 per cent. acid. With the second and third fractions the specific gravity decreases with 98 per cent. acid treatment, the effect being more marked in the third fraction.

The conclusions reached as a result of this work are :—

(1) That any attempt to estimate either aromatic or olefinic hydrocarbons by any method based upon changes in specific gravity must lead to fallacious results.

(2) That 80 per cent. acid treatment is inadequate for the complete removal of olefines.

(3) That it is desirable to fractionate a spirit into fractions such as those indicated in order to render possible the removal of polymers produced by acid treatment, such removal not being possible when the spirit is treated as a whole.

Further experiments are in hand regarding the strength of acid necessary for the more complete removal of the olefines.

During the estimation of aromatic hydrocarbons in a similar cracked benzine in which the aniline point was taken after washing first with 80 per cent. acid, and then with what was thought to be 100 per cent. acid, but which was subsequently found to be equivalent to 101 per cent., it was found that losses occurred on treatment with the stronger acid, which were out of all proportion to the aromatic hydrocarbon content as determined by the aniline point method. The results were obtained by the treatment of a refined pressure cracked benzine made from a residue from a paraffin base crude. The benzine had the following properties :—

S.G. @ 15·5° C. .. .. 0·728

DISTILLATION TEST.

I B.P.	37° C.
To 100° C.	32·5%
100—150° C.	46·5%
150—189° C.	19·0%
F.B.P.	189° C.
Bromine absorption (Johannsen), 22·6 grams/100 grams.	
Gum value 0·0018 grams/100 c.c.s.	

The results obtained were as follows :—

TABLE III.

Original S.G. @ 15·5° C.	0·728	
Volume loss to 80% H_2SO_4	3·0%	
S.G. after treatment	0·730	
Additional loss to 101% H_2SO_4	27·0%	by vol.
S.G. after treatment	0·722	
Aniline point of original benzine	53·5° C.	
" " after 80% acid	54·5° C.	
" " " 101% acid	68·5° C.	
Aromatic content of supposed olefine free	16·4%	
Loss in weight due to 101% H_2SO_4 treatment	28·6%	

The heavy loss to 101 per cent. acid, compared with the aromatic hydrocarbon content will be noted. Some of this loss with 101 per cent. acid is undoubtedly due to the removal of olefines, which as has been previously shown, are not completely removed by 80 per cent. acid. As the authors were not satisfied that the loss with 101 per cent. acid was not entirely attributable to this cause it was decided to treat the benzine with 80 per cent. acid, followed by washes of 100 per cent. and 101 per cent. acid. The method of procedure was as follows :—

A known volume of the benzine was treated with 80 per cent. acid and the following data determined, loss in volume, specific gravity, and aniline point. Washing with 100 per cent. acid was then carried out as previously described for 98 per cent. acid, and the same data redetermined. After this a succession of washes of 100 per cent. by volume of 101 per cent. acid, were given so long as any changes in the aniline point or volume occurred.

The results obtained in these tests were :—

TABLE IV.

Original S.G. @ 15·5° C.	0·728
80% acid treatment.	
Volume loss to 80% acid	3·0%
S.G. @ 15·5° C. after treatment	0·730
Aniline point	53·6° C.
100% acid treatment.	
Additional volume loss to 100% acid	16·0%
S.G. @ 15·5° C. after treatment	0·721
Aniline point	66·2° C.

Aromatic hydrocarbon content from the above data.

(1) On supposed olefine free (A.P.) .. .. .. 14·5% weight
(2) „ „ „ „ (by loss in weight) .. 17·5% „
(1) Calculated to the original benzine .. .. .. 14·1% „

Treatments with 101% *acid.*

Treatment No.	Additional volume loss %	S.G. after treatment.	Aniline point.
1	4·6	0·721	67·8
2	6·0	0·722	68·2
3	6·0	0·722	69·0
4	6·0	0·723	69·8
5	6·0	0·723	70·4
6	—	0·723	70·4

Similar results were obtained with a crude pressure-cracked benzine from a non-paraffin base residue. In view of the results obtained with these cracked benzines it was decided to submit three commercial benzines to identical treatments. The results obtained together with those obtained on the above-mentioned cracked benzines are given in the following table :—

TABULATED RESULTS.

TABLE V.

	No. 1 Benzine from paraffin base residue.	No. 2 Benzine from non-paraffin base residue.	Shell Nol 1.	B.P. No. 1.	Pratt's No. 1.
Original S.G. benzine	0·728	0·730	0·744	0·730	0·730
80% *acid treatment.*					
% Vol. loss ..	3·0	6·5	Nil.	Nil.	Nil.
S.G. after treatment	0·730	0·736	0·744	0·730	0·730
Aniline point °C. ..	53·6	52·2	46·1	54·0	53·6
100% *acid treatment.*					
% Vol. loss ..	16·0	17·0	11·0	12·0	7·0
S.G. after treatment	0·721	0·717	0·730	0·714	0·725
Aniline point °C. ..	66·2	67·5	58·2	64·6	58·9
% Aromatics on supposed olefine free	14·5	17·3	13·8	12·25	6·25
% Aromatics on original	14·1	16·3	13·8	12·25	6·25
101% *acid treatment* (final results).					
% Vol. loss ..	28·6	25·0	2·3	Nil.	10·2
S.G. after treatment	0·723	0·717	0·732	0·716	0·728
Aniline Point °C. ..	70·4	74·0	58·4	64·9	60·0

It will be noted that benzines No. 1, No. 2 and Pratt's No. 1 are similar with respect to their behaviour with 101 per cent. sulphuric acid, following upon treatment with 100 per cent. acid.

Each suffers a loss in volume accompanied by little change in the specific gravity, but by a distinct increase in the aniline point. In the case of the Shell No. 1 and B.P. No. 1 benzines, the changes due to treatment with 101 per cent. acid are slight. Since Pratt's No. 1 benzine probably contains hydrocarbons produced by cracking, it resembles the entire cracked benzines rather than the Shell No. 1 and B.P. No. 1, which are probably free from cracked benzine.

The loss in volume accompanied by little change in specific gravity resulting from the treatment with 101 per cent. acid, cannot be attributed to the removal of aromatic hydrocarbons or cycloparaffins, since these have specific gravities much higher than those of the residuum from the treatment with 100 per cent. Also the removal of such quantities of either of these classes of hydrocarbons would result in a much greater increase in the aniline point. Furthermore, since it is highly improbable that any olefines survive treatment with 100 per cent. acid, it is concluded that certain paraffins present in cracked benzine are more readily attacked by strong sulphuric acid than those present in straight run benzines. Since the absorption or treatment with 101 per cent. acid terminates and does not continue indefinitely it cannot be due to general attack upon the paraffins. It is known that, although normal paraffins are attacked by fuming sulphuric acid at 100° C. and the gaseous ones, such as butane, at room temperatures (Brennstoff-Chimie, 1925, 6, 169—177) tertiary paraffins, such as di-isopropyl $(CH_3)_2CH : CH(CH_3)_2$, are more readily sulphonated and oxidised than normal paraffins. That cracked benzines contain tertiary and iso-paraffins is suggested as an explanation of the phenomena noted above. Cracked benzine is doubtless partly produced by the coalescing of molecular fragments and this would explain the presence of paraffins other than those of the normal type.

It should be noted that the specific gravities of the isomeric paraffins differ little from one another, a point in explanation of the change in volume without appreciable change in specific gravity.

Attention is directed to the markedly higher aniline points of the cracked benzine after treatment with 101 per cent. acid compared with those of the three commercial samples after the same treatment. No evidence could be found in literature as to the effect upon the aniline point of isomerism.

In conclusion, the authors wish to tender their thanks to the Directors of Messrs. Vickers, Ltd., for their kind permission in allowing these notes to be published.

Mr. E. C. Craven said he would endeavour not to add to the difficulties of the matter by reading out lists of figures, but would draw one or two diagrams which would make what he had to say

quite clear. He restricted his remarks to a cracked spirit supplied by Mr. Lomax. He would plot the acid strength against the losses and various other characteristics of the residual spirits. He had started with acid of 80 per cent. strength, and had gone to just over 100 per cent. For that cracked spirit the acid losses by weight followed a smooth curve.

Here curves, which would be submitted for publication in the Journal,* were drawn on the blackboard, showing the effect of single and double washings with sulphuric acids of strengths from 80 per cent. to 101 per cent. The double washing curve ran parallel to that for a single washing, but a little above it. The density curve showed a maximum at 88 per cent. sulphuric strength.

The refractive indices followed exactly the same curve. When they were plotted to be on the same scale they could not be distinguished. The aniline points, on the other hand, followed a smooth curve. That maximum point for density and refractive index, he was informed by Mr. Harold Moore, also corresponded to the point at which the iodine absorption of the residual spirit was nought; so that if there was any critical strength of sulphuric acid at all it was somewhere about 88 per cent. His absorption curve was completely different from that obtained by Dr. Dunstan.

Dr. Dunstan, interrupting, said his curve was after distillation.

Mr. Craven, continuing, said that from the density and refractive index, after the removal of unsaturateds, and presumably the aromatics, by 99 per cent. sulphuric acid, the relative proportions of naphthenes and paraffins could be calculated. The proportion of naphthenes and paraffins after treatment with acid over 100 per cent. strength did not vary very much. He thought the explanation of the small changes in density, and so forth, was that the paraffins and naphthenes were being attacked very much as a whole by the free SO_3.

Mr. Harold Moore remarked that Mr. R. B. Hobson and himself had been making some investigations on a cracked spirit, and they had been much troubled about the concentration of acid required to remove the olefines without the removal of aromatics. Assuming that the iodine value was not a correct reading of the unsaturated hydrocarbons present, it was only reasonable to assume that it would be roughly proportional to the unsaturateds present after various acid washes. Mr. Hobson and himself therefore had made washes with various concentrations of acid of 80, 85, 90 and 95 per cent., with various quantities up to 15 volumes, and with various periods of treatment. The figures

* See "Observations on the Action of Sulphuric Acid on Petrol." This Journal, pp. 67-75.

appeared in a paper in the Journal.* The periods varied up to 70 to 100 hours. First of all the iodine value had been determined, and then the reductions of the iodine value by the various concentrations of acid, and they had found that an 80 per cent. acid strength only reduced the iodine value by about 32 per cent. of the original value; that was to say, it accounted for roughly 32 per cent. of the unsaturateds being removed. With very large quantities running up to 18 volumes of acid and exposing for over 100 hours, 80 per cent. acid removed roughly 55 per cent. of the iodine value; that is to say, of the unsaturateds. Using 85 per cent. acid, in large quantities and over long periods, about 68 per cent. was removed; and with 90 per cent. acid and treatment for 48 hours, 96·3 per cent. of the iodine value was removed. With 98 per cent. acid—removing aromatics as well—100 per cent. of the unsaturated was removed. 96·3 per cent. was considered a sufficiently complete extraction for practical purposes. They did not want to go too far because of the fear of removing the aromatics at the same time. The aromatics had been calculated (the method appeared in the paper referred to), and the spirit contained, as far as could be ascertained, about 5·1 per cent. of aromatics, and of the 5·1 per cent. about 1 per cent. was removed by the 90 per cent. acid. Personally he thought that about 88 per cent. would be the optimum acid concentration, not going quite as high as 96 per cent., on account of the fear of removing aromatics.

They had wanted to know what the effect on the aniline cloud point would be of a given percentage removal of unsaturateds. Then, together with the effect on the aniline cloud point of the removal of aromatics, it would only be necessary to determine for practical purposes the aniline cloud difference with 98 per cent. sulphuric acid, and the iodine value; and by calculation they could get the percentage of both olefines and aromatics present. They had therefore determined the influence of the removal of unsaturateds on the aniline cloud point at the low end of the acid concentration. At 90 per cent. it was feared aromatics might be removed, but at 80 per cent. they were only very incompletely removing olefines, and were therefore fairly safe in thinking that aromatics were not removed. Therefore a constant had to be determined for the rise in aniline cloud point, dependent on a given percentage of unsaturateds, and it had been found that 1° C. aniline cloud test corresponded in that particular spirit to 2·59 per cent. of unsaturateds.

Prof. Brame asked whether the polymers were removed by distillation before the aniline points were taken.

Mr. Harold Moore replied in the affirmative. They had re-

* Vol. II, No. 53, pp. 587-592, Dec., 1925.

moved them in the experiment to which he was referring, but that constant of 2·59 per cent. would, he was afraid, be affected by naphthene content, because the range over which one might move the aniline cloud point from maximum to minimum with acid concentrations was dependent on the naphthene content. In that particular spirit there was 50 per cent. of naphthenes. It might not be quite accurate, but it was a fairly simple way of determining the constant of 2·59 per cent (roughly 2·6 per cent.) for the effect of unsaturateds on the aniline cloud test. The constant was of use when dealing with spirits of such a kind—as a rough measure at all events.

Prof. Brame, in reply, said he desired to emphasise the desirability of getting as full an account as possible of the work which the members could lay before the Institution put into the Journal, even if they had not had the opportunity of speaking that night. This would be of immense value, because what had been said by the limited number of speakers that night did emphasise what a difficult problem they were up against, and the Institution would like to have the matter as thoroughly thrashed out as possible, because it was of vital importance on account of the increased use of cracked spirits and blends of cracked spirit.

One of the important points which had been brought out in the discussion was the question of the strength of the acid which should be used for polymerising, etc., the unsaturated hydrocarbons. Personally, he had had the temerity to suggest 84·5 per cent. as agreeing with the definite hydrate, but he had mentioned that it had not proved that stronger acid might not give further action. From Dr. Dunstan's remarks, which had been supported by what Mr. Harold Moore had said, probably a stronger acid—about 88 to 90 per cent.—would ultimately prove the best.

The most interesting point perhaps in Dr. Dunstan's remarks had been the fact that he had got a maximum in the curve. He wished to emphasise, however, that the curve which he had drawn showing the maximum at 88 per cent., was not a diminution in volume curve simply, but was obtained by distillation within the original range after treatment with acid.

The President, having thanked Prof. Brame for opening the discussion on the matter, the Meeting adjourned.

The following was subsequently received from **Dr. F. H. Garner :** In the treatment of cracked spirit with sulphuric acid for the removal and polymerisation of olefines, there appears to be a possibility of the simultaneous removal of a proportion of the aromatic hydrocarbons present. Thus, Brochet (Bull. Soc. Chim., 1893, 9, 867) found that normal hexylene reacts with benzene in

the presence of 66° Beaumé (93 per cent.) sulphuric acid giving a yield of about 50 per cent. of hexylbenzene. The course of the reaction appears to be first the formation of a hexyl sulphonic acid, which then reacts with benzene to give the hexylbenzene. Amylenes behave in a similar way, but give lower yields owing to the formation of a large proportion of acid tar, and toluene behaves in the same manner as benzene.

It is thus necessary to ascertain that sulphuric acid, in the concentration used for the removal of olefines, is not only without action on aromatic hydrocarbons, but also that it is also without action on aromatic hydrocarbons *in the presence of olefines*. If the reaction described above does occur in the treatment of cracked spirit with sulphuric acid of the lower concentrations used in the removal of olefines, then the estimate of aromatic hydrocarbons will be too low by this method.

Observations on the Action of Sulphuric Acid on Petrol.

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., and
E. C. Craven, B.Sc., F.C.S.

The binary mixture of sulphuric acid and water of minimum boiling point contains 98·3% by weight of sulphuric acid. The reagent acid as bought from the dealers is usually about of this strength. In the following work stronger acids were prepared by the addition of fuming acid. Acid strengths given in all cases by weight were determined by titration of weighed portions of pure dry sodium carbonate.

The determination of loss of weight of petroleum spirits when shaken out with acid was carried out as follows :—

A 250 c.c. separating funnel was shaken out with the spirit under test, allowed to stand for an hour, then run out and drained for 5 mins. This corrects for the evaporation loss amounting to about 0·2% which would otherwise take place in the funnel. 50 cc. of the spirit were then weighed into the funnel and 150 cc. of acid poured in. The funnel was shaken gently for half an hour on a mechanical shaker, allowed to stand 20 hours, the acid run off as carefully and completely as possible and the residual spirit run into a weighed bottle, draining 5 minutes. Losses of spirit occur in pouring in and by evaporation in the air drawn in by the outflowing acid and no doubt in other ways. An attempt was made to correct for these handling losses by doing blank experiments without acid. These evaporation losses naturally make the determination of acid loss somewhat uncertain. Possibly an accuracy of 0·5% is all that can reasonably be claimed.

It would probably be well if in work on this subject the 3—1 ratio of acid with half an hour shaking were adhered to, so as to conform to the conditions of the Thole, Tizard and Marshall, Chevanne and Simon tests.

Aniline points were corrected for the water content of the aniline (see previous note). The following tables show the results obtained :—

Pratt's No. 1.

(Evaporation loss = 0·75%.)

H_2SO_4 % wt.	Loss % wt.	d 20° C.	nD 20° C.	Aniline pt. °C.
Original spirit		0·7262	1·4064	53·0° C.
79·1	0·7	0·7276	1·4072	53·2
84·2	1·0	0·7285	1·4162	53·4

H_2SO_4	Loss	d 20° C.	nD 20° C.	Aniline pt.
89·5	1·9	0·7286	1·4161	54·3
92·0	3·4	0·7257	1·4058	55·8
93·8	5·7	0·7236	1·4043	57·4
95·4	6·8	0·7211	1·4030	59·0
97·6	7·8	0·7199	1·4018	59·0
98·6	8·3	—	—	59·3
99·7	8·3	0·7197	1·4019	59·3
100·5	16·3	0·7187	1·4020	59·9

A large quantity of the above Pratt's No. 1 spirit was washed out with 3 volumes of 98·6% acid. Tests made on the aromatic freed spirit gave the following results :—

PRATT'S RESIDUE (Aromatic Freed Spirit).

(Evaporation loss = 0·5%.)

H_2SO_4. % wt.	Loss % wt.	d 20° C.	nD 20° C.	Aniline pt. ° C.
Original spirit		0·7217	1·4032	58·9
80·9	nil	0·7218	1·4039	58·9
85·4	nil	0·7218	1·4038	58·9
88·5	0·3	0·7216	1·4037	58·9
98·0	0·8	0·7225	1·4037	59·0
99·7	1·8	0·7218	1·4032	59·3
101·4	14·2	0·7206	1·4034	60·6

As it seemed curious that further loss should occur with 98% acid, some of the residue was washed repeatedly with acid of 97·7% strength. The losses were as follows :—

	% Loss.
1st washing	0·4
2nd ,, ...	0·4
3rd ,, ...	0·3
4th ,, ...	0·4
5th ,, ...	0·3 (48 hours settling)

The smallness of the above losses makes it doubtful if further action is taking place ; possibly the evaporation loss allowance is too small.

CRACKED SPIRIT.

This was supplied by Mr. E. L. LOMAX.

(Evaporation loss = 0·4%.)

H_2SO_4 % wt.	Loss % wt.	d 20° C.	nD 20° C.	Aniline pt. ° C.
Original spirit		0·7248	1·4084	51·1
79·1	2·5	0·7295	1·4110	53·1
84·2	3·1	0·7333	1·4128	54·6
89·5	5·5	0·7342	1·4132	56·9
91·9	8·2	0·7302	1·4106	59·3
94·5	11·1	0·7262	1·4083	61·0
96·2	13·6	0·7218	1·4057	62·7
97·7	15·4	0·7185	1·4037	63·8
99·7	19·2	0·7151	1·4016	64·6
100·5	23·5	0·7126	1·4006	64·5

This experiment was repeated, giving two successive washings with each strength of acid.

(Evaporation loss $2 \times 0{\cdot}4\% = 0{\cdot}8\%$.)

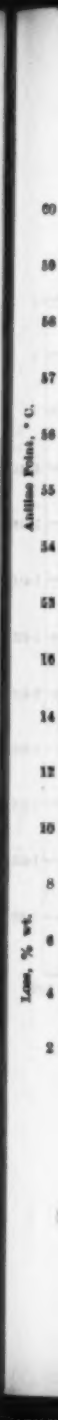
H_2SO_4 % wt.	Loss % wt.	do 20° C.	nD 20° C.	Aniline pt. °C.
80·2	3·5	0·7308	1·4115	53·6
84·9	3·8	0·7345	1·4138	55·2
90·1	6·5	0·7334	1·4124	57·8
91·9	8·8	0·7301	1·4104	59·5
93·7	11·5	0·7262	1·4083	61·4
95·8	13·5	0·7221	1·4056	62·8
97·8	16·2	0·7182	1·4035	64·1
99·6	20·9	0·7135	1·4009	65·2
100·2	29·5	0·7107	1·4000	65·8

The figures are shown in the accompanying graphs. It will be noticed that the acid loss curves are for the most part fairly smooth, showing no distinct breaks. In the case of the No. 1 spirit, however, there is some indication of complete removal of unsaturateds and aromatics at about 98% strength of acid. The density and refractive index rise till the acid strength is about 88%. This is no doubt due to polymerisation and removal of unsaturateds. At higher strengths of acid extractions of aromatics goes on and the density and refractive index fall. Hence the strength of 88% H_2SO_4 appears to be where the extraction of unsaturateds is completing and the extraction of the aromatics commencing.

This is confirmed by the experiments of Moore and Hobson (Journal 11, 592, 1926), who find that a strength of 88%—90% is essential for the removal of unsaturateds.

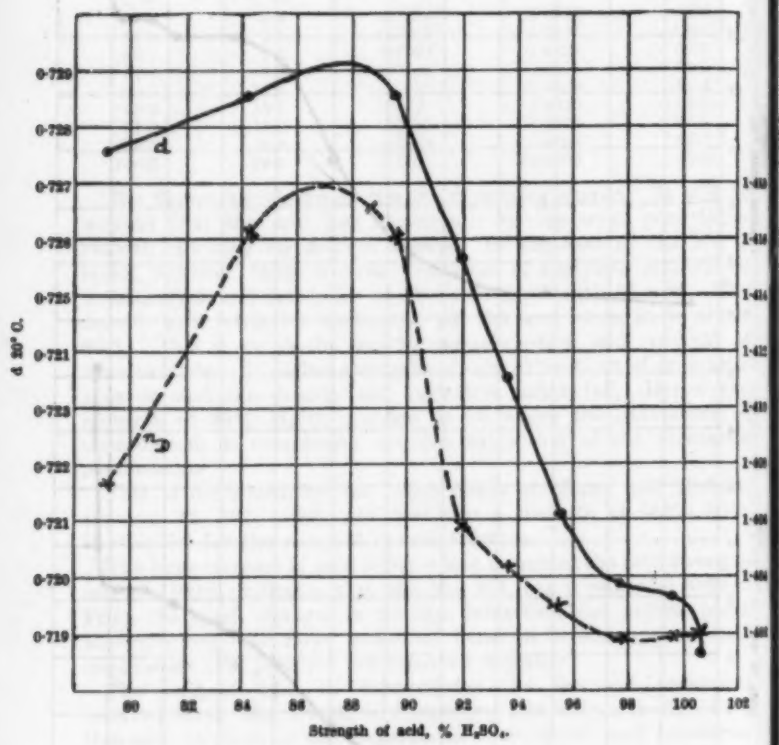
The huge increase in acid losses which occurs as the acid strength exceeds 100% indicates that the free SO_3 has a powerful action. From the small changes in density, refraction and aniline point accompanying the large increased losses it would appear that naphthenes and paraffins are removed together.

The authors wish to acknowledge the financial assistance received from the Distillers Company, Limited, and the Fuel Research Division of the Department of Scientific and Industrial Research towards the expenses of this research.



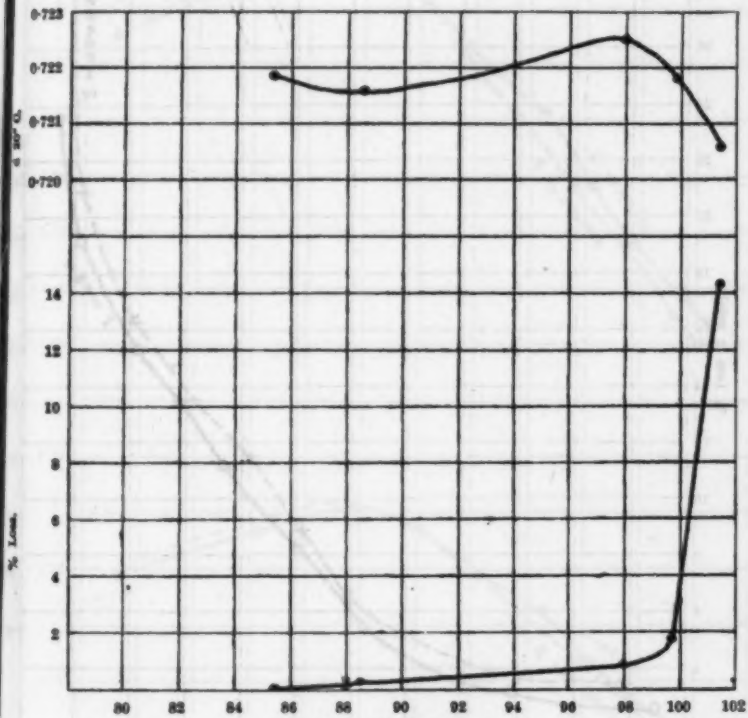
PRATT'S NO. 1 PETROL.

ANILINE-POINT AND LOSS.



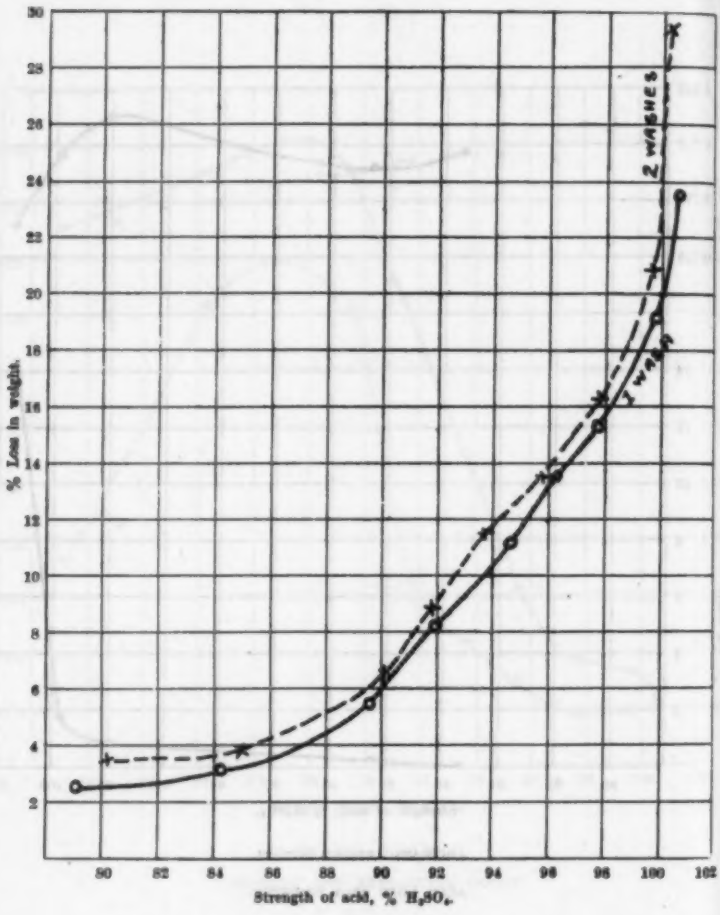
PRATT'S NO. 1 PETROL.

DENSITY AND REFRACTIVE INDEX.



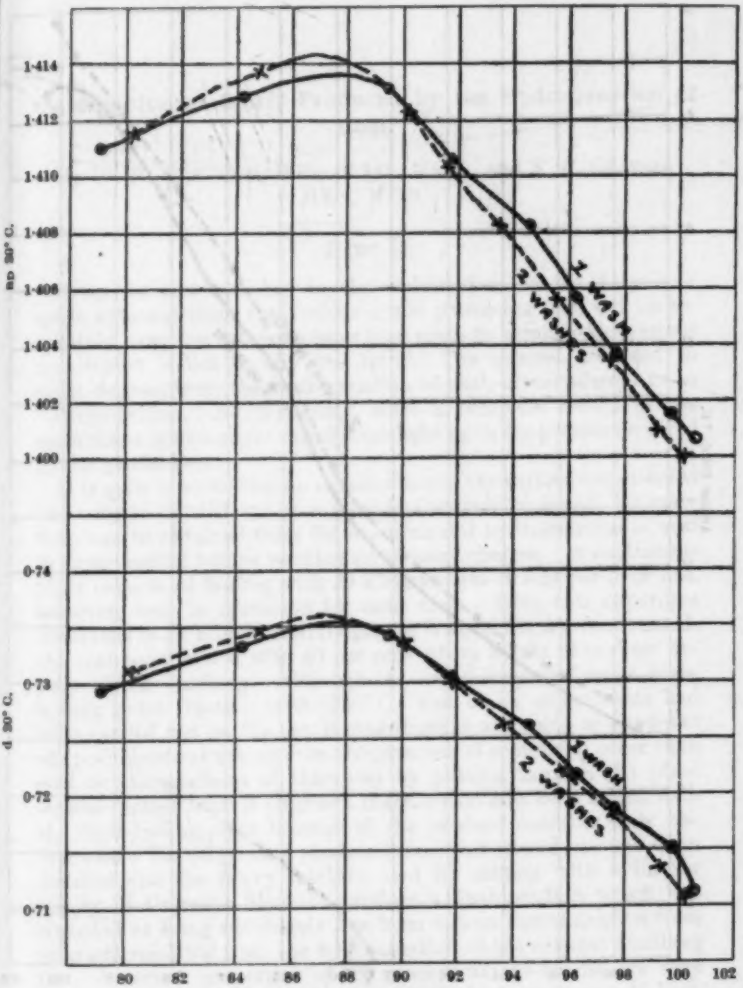
AROMATIC FREED SPIRIT.

ACID LOSS AND DENSITY.



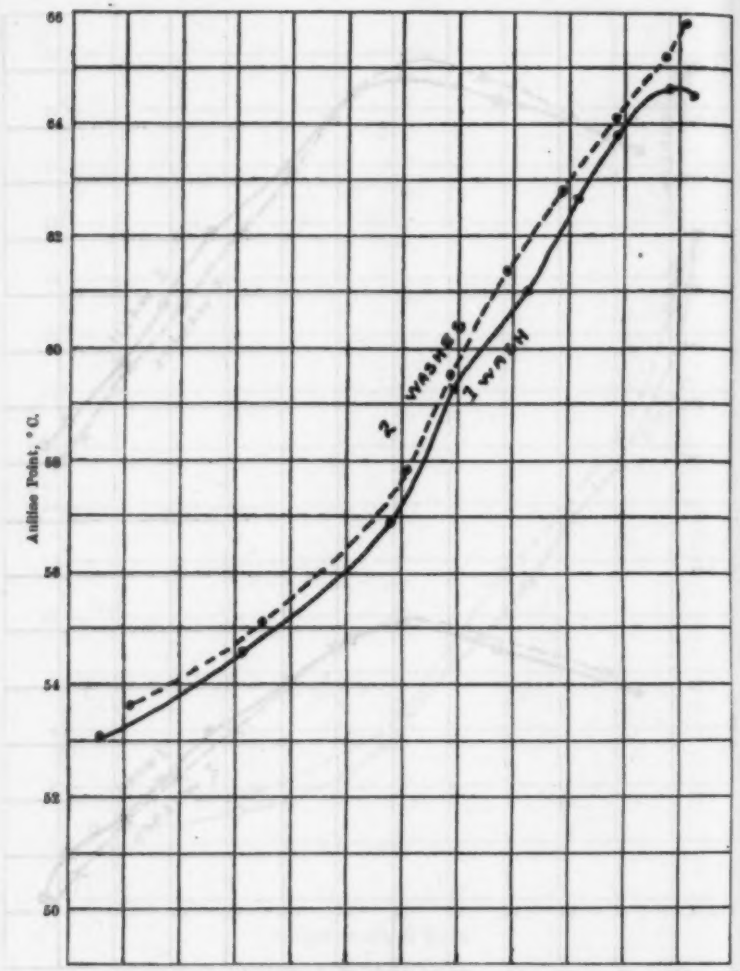
LOMAX CRACKED SPIRIT.

ACID LOSSES.



LOMAX CRACKED SPIRIT.

REFRACTIVE INDICES AND DENSITIES.



LOMAX CRACKED SPIRIT.

ANILINE POINTS.

Examination of Spirit Produced by the Hydrogenation of Coal.

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven, B.Sc., F.C.S.

Part I.

Great interest attaches to the constitution of the petroleum spirit obtained from the various crude petroleum oils, but unfortunately, very few attempts have been made to separate the various constituent bodies in any one spirit. The interest attached to spirit derived from the hydrogenation of coal, often referred to as "Berginisation," is very great, since a complete record of the constituent bodies might throw some light upon the process involved in the production.

It is quite obvious that an examination of the various constituents can only be carried out on a considerable bulk of liquid, far more than can be obtained from the experimental hydrogenation of coal in experimental bombs working on isolated charges. A continuous plant capable of dealing with 20 kilogrammes of coal per hour has, however, been in operation for some time. With this apparatus some tons of an English coal (Orgreave Washed Slack) were treated, the coal being mixed with 40 per cent. of its weight of coal tar obtained from Duisberg. Although the tar so employed was a high-boiling point fraction (250—350° C.) and blank experiments had been carried out on the tar, it was thought advisable to eliminate the possible errors arising from the presence of something other than coal or the products of that coal by putting through the plant several further tons of Orgreave Slack which had been mixed with the high boiling-point fraction of the product resulting from the first run. The oil product produced from this second run was again distilled and the heavy fraction used for mixing with a further supply of Orgreave Slack to produce a final product which was regarded as being adequately free from serious contamination from products resulting from the hydrogenation of the original Duisberg tar. A certain proportion of the gases from the condensers were passed through activated charcoal, and the hydrocarbons held back by that charcoal were displaced by steaming. The total spirit produced formed approximately 10 per cent. of the weight of the coal passed through the hydrogenation plant.

The spirit, as received, was a mobile pale yellow fluid, having to a small degree the odour associated with cracked spirit. It was slightly "gassy," pointing to the presence of a proportion of very low-boiling point constituents.

Before commencing any work on the spirit it was washed repeatedly with dilute caustic soda and dilute sulphuric acid. The treatment removed small quantities of phenolic and basic substances, which were not further examined. This loss amounted to about 1 per cent. in all, including washing losses. All succeeding work was done on this washed stock spirit. Temperature measurements in distillation were carried out throughout by means of a bare copper-eureka thermo-couple, as described in a previous paper (*Journal* 10, 43, 1924), in order to avoid thermometric lag.

WASHED SPIRIT.

$d_{20°\,C.}$	0·7055
$n_{D}20°$ C.	1·3974

"ENGLER" DISTILLATION.

Drop A	40·2° C.	50% over	78·3° C.
„ B	40·7	60% „	84·7
1% over	44·3	70% „	92·4
2% „	46·3	80% „	105·3
5% „	48·5	90% „	123·5
10% „	52·7	95% „	158·3
20% „	59·2	Dry „	160·0
30% „	65·4	Residue	1·5%
40% „	72·1	Loss	2·0%

Free sulphur .. .. .. 30 mg. per 100 cc.
Iodine absorption .. .. .. =7·8% (Hanus test).

If we assume the unsaturateds to absorb I_2 and have a mean molecular weight of 100, the proportion of unsaturateds worked out at 3·1 per cent.

A rough determination of aromatic hydrocarbons was carried out by the Tizard-Marshall method.

Aniline point of stock spirit	47·0° C.
Ditto, after washing with 80% H_2SO_4	48·0°
Ditto, „ „ 98% H_2SO_4	54·5

The analysis is thus :—

Unsaturateds	3·1%
Aromatics	7·6%
Naphthenes	51·7%
Paraffins (by diff.)	37·6%

The small increase of aniline point by washing with 3 volumes of 80 per cent. sulphuric acid shows the content of unsaturated hydrocarbons to be low.

The residue of naphthenes and paraffins after the strong sulphuric wash showed :—

d_{20}° C.	0·7038
n_{D}20° C.	1·3950

The specific refractivity (r_o) is thus 0·5611. From this the naphthene content would be about 60 per cent. (*vide Journal* 10, 41, 1924).

Determination of Individual Aromatics.

500 gms. of stock spirit were carefully fractionated through an 8-bulb Young " Evaporator " column, and gave :—

	°C.	g.	%
Fraction 1	to 55 ..	162·6 ..	23·2
,, 2	95 ..	240·9 ..	48·2
,, 3	122 ..	65·5 ..	13·1
Residue	— ..	45·6 ..	9·1
		Total ..	93·6

Fraction 1 was set aside as not containing aromatics. The aniline points on the other fractions : (*a*) direct ; (*b*) after 80 per cent. H_2SO_4 ; (*c*) after 98 per cent. H_2SO_4, were :—

	a. °C.	*b.* °C.	*c.* °C.
Fraction 2	45·0 ..	46·2 ..	50·7
,, 3	— ..	39·5 ..	51·8
Residue	— ..	30·7 ..	60·6

Calculation from these figures gives the following results :—

		%		%
Fraction 2 ..	Benzene =	2·65	Naphthenes =	24·1
,, 3 ..	Toluene =	1·85	,, =	8·0
Residue ..	Xylol, etc. =	2·85	,, =	4·2
Total aromatics		7·35	Total	36·3

The percentages are, of course, on the original spirit.

1000 gms. of stock spirit were now taken for systematic fractional distillation. Four fractions were made first of all, as follows :—

(1) to 55° C. (2) to 95° C. (3) to 122° C. (4) to Residue.

The iodine number of each fraction was determined and the whole fraction shaken out with 3 volumes of strong sulphuric acid. After standing overnight the unattacked spirit was separated and weighed. By guessing the mean molecular weight of the unsaturated hydro-

carbons present in each fraction the aromatics could be calculated by difference as follows :—

	% wt.	Acid loss. %	I. No.	Unsaturateds. Mol. wt. %	Aromatics. %
Fraction 1 ..	21·8	1·6	13·8	70 (?)=0·8	(0·8)
,, 2 ..	46·8	4·5	10·2	90 (?)=1·7	2·8
,, 3 ..	17·7	2·8	8·7	110 (?)=0·7	2·1
Residue ..	8·2	3·2	6·0	130 (?)=0·2	3·0
				3·4	7·9

It will be noticed the unsaturateds appear to be evenly spread over the four fractions and that the proportions of aromatic hydrocarbons found by more direct methods are confirmed.

It may be mentioned here that, from similar fractions of another portion of stock spirit, Fractions 2 and 3 gave good crops of dinitrobenzene and 1, 2 and 4 dinitrotoluene respectively. From the residue a large quantity of nitro bodies was obtained as an oil from which the only body which would crystallise was dinitronaphthalene. From the residue fraction of the 1000 gm. lot a small amount of elementary sulphur crystallised out.

It now remained simply to carry on the tedious process of fractionation in order, if possible, to identify the paraffins and naphthenes present with special reference to the saturated hydroaromatics. The fractionation was made first into 5° C. fractions, and then into 2° C. and 1° C. fractions. After this fourth fractionation the fractions were weighed and their density and refractive index determined. The results are shown graphically. Another four fractionations were now made retaining the 1° C. interval and the results of these further fractionations are also shown graphically.

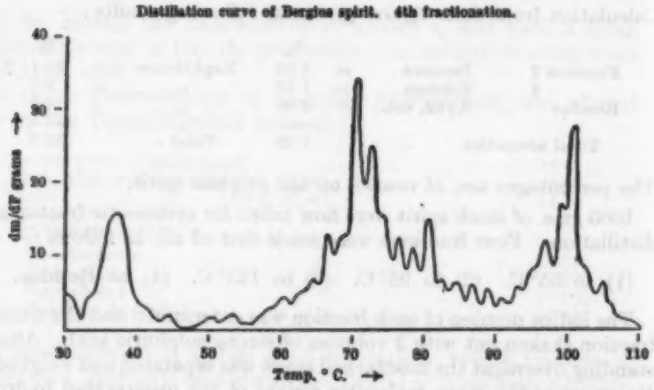


FIG. 1.

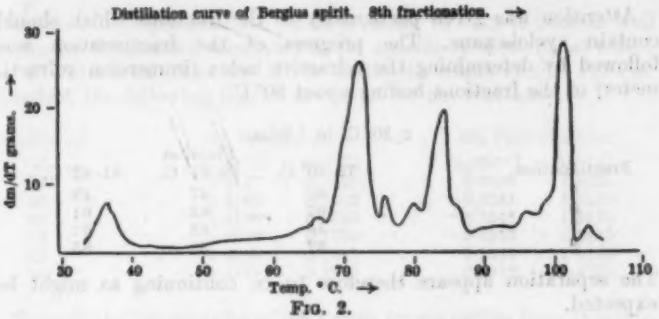


FIG. 2.

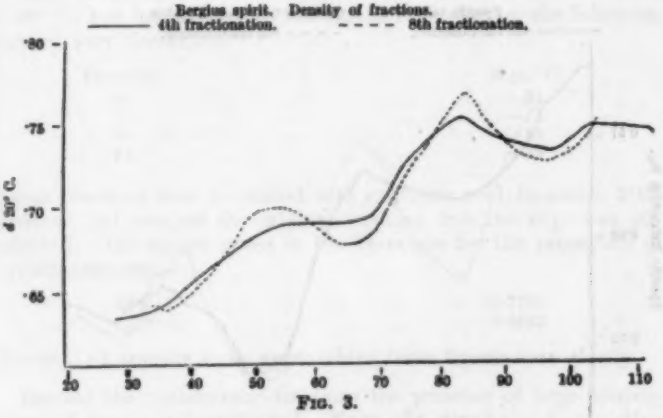


FIG. 3.

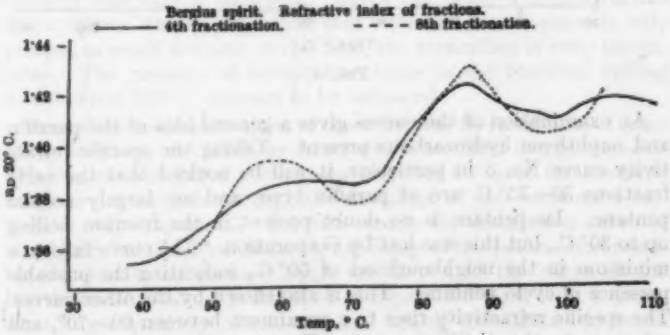


FIG. 4.

Attention was given particularly to the fractions which should contain cyclohexane. The progress of the fractionation was followed by determining the refractive index (immersion refractimeter) of the fractions boiling about 80° C.

	n_D20° C. in ° Zeiss.		
Fractionation.	Fraction 79–80° C.	80–81° C.	81–82° C.
4	40 ..	47 ..	49
6	67 ..	62 ..	61
7	86 ..	63 ..	67
8	52 ..	59 ..	65

The separation appears therefore to be continuing as might be expected.

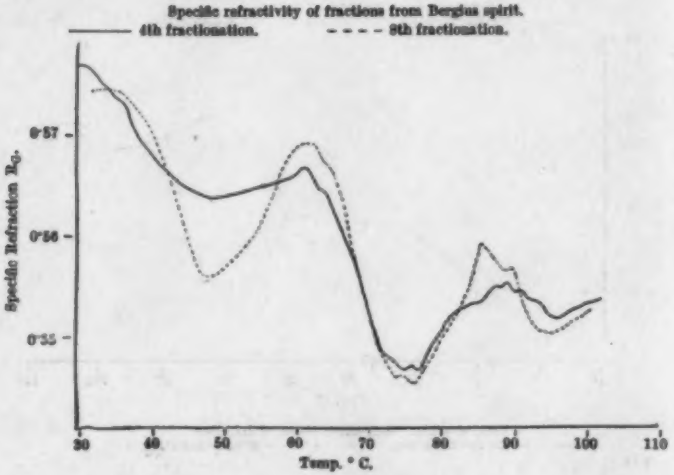


FIG. 5.

An examination of the curves gives a general idea of the paraffin and naphthene hydrocarbons present. Taking the specific refractivity curve No. 5 in particular, it will be noticed that the early fractions 30—35° C. are of paraffin type, and are largely normal pentane. Iso-pentane is no doubt present in the fraction boiling up to 30° C., but this was lost by evaporation. The curve falls to a minimum in the neighbourhood of 50° C., indicating the probable presence of cyclo pentane. This is also shown by the other curves. The specific refractivity rises to a maximum between 60—70°, and reference to the distillation curves, particularly No. 1, shows the

presence of several hexanes. The presence of cyclohexane is well shown by the marked minimum in the specific refractivity at about 81° C. Since this was one of the bodies to which special interest attaches, the following figures are given for the fractions :—

Fraction to	3th Fractionation.		4th Fractionation.	
° C.	n_D20° C.	d20° C.	n_D20° C.	d20° C.
79	1·4137	0·7536 ..	0·7506	1·4128
80	1·4168	0·7592 ..	0·7534	1·4120
81	1·4196	0·7645 ..	0·7548	1·4148
82	1·4221	0·7700 ..	0·7552	1·4155
83	1·4218	0·7688 ..	0·7538	1·4140
84	1·4189	0·7615 ..	0·7512	1·4136

None of the fractions from the fourth fractionation froze down to —40° C., but for those from the eighth fractionation the following figures were found :—

Fraction.	M.p. ° C.
81	—31
82	—13
83	—15
84	—35

These fractions were re-treated with sulphuric acid, in case a little benzene had escaped the original washing, but the m.p. was unaffected. The figures given in the literature for the properties of cyclohexane are :—

d20° C.	0·7781
n_D20° C.	1·4263

Fraction 82 appears to be approaching these figures very closely.

Beyond the cyclohexane fractions the presence of large proportions of heptanes is indicated. From the density and refractive index figures it may be judged that either normal heptane is only present in small amount or else that the separation is very incomplete. The presence of hexahydrotoluene in the fractions boiling round about 102° C. appears to be indicated.

One of the main difficulties of the work was the smallness of some of the fractions and the large losses which occurred due to unavoidable evaporation losses. When the fractions are small the amounts hung up in the column and the drainings of the condenser, etc. become very important. For this reason the distillation curve of the eighth fractionation lacks a good many of the peaks corresponding to definite substances which are shown in the curve of the fourth fractionation. It is hoped to repeat the work with a somewhat larger quantity of material and taking precautions to avoid losses as far as possible.

Part II.

The distillation of the aromatic freed spirit was repeated, starting with 3 litres. An iced-cooled copper spiral condenser was used, and the fractions up to 85° C. or so were stored in an iced box. In spite of these precautions evaporation losses to the extent of rather more than 30 per cent. took place. An approximate correction for these losses is made in the final calculations by taking the volumes of the fractions collected as masses. The temperature measurements were made by a thermo couple as before, and the figures given below are after twelve fractionations in most cases, and fourteen in parts :—

Fraction no.	To ° C.	Vol. c.c.	d20° C.	n_D20° C.	% naphthenes.
7 ..	30·0	250	—	—	—
8 ..	32·0	25	—	—	—
9 ..	35·2	105	0·6262	1·3577	—
10 ..	37·4	79	0·6252	1·3571	—
11 ..	39·6	30	0·6280	1·3583	—
12 ..	41·9	3	—	—	—
13 ..	44·0	7	—	—	11·4
14 ..	46·0	2	From previous work		29·5
15 ..	48·2	3	—	—	47·6
16 ..	50·4	11	0·7238	1·3988	84·0
17 ..	52·6	13	0·7202	1·3978	77·0
18 ..	54·8	8	—	—	—
19 ..	55·3	9	0·6982	1·3803	50·2
20 ..	56·8	5	—	1·3858	—
21 ..	58·6	4	—	1·3813	—
22 ..	60·4	20	0·6630	1·3760	—
23 ..	62·3	34	0·6579	1·3738	—
24 ..	64·1	29	0·6598	1·3738	3·6
25 ..	65·9	28	0·6642	1·3768	—
26 ..	67·7	19	0·6680	1·3785	3·2
27 ..	69·5	213	0·6837	1·3849	21·8
28 ..	71·4	86	0·7062	1·3941	47·6
29 ..	73·2	13	0·7309	1·4043	73·0
30 ..	75·0	7	0·7429	1·4096	82·3
31 ..	76·8	16	0·7526	1·4145	84·9
32 ..	78·6	13	0·7617	1·4187	90·6
33 ..	80·4	87	0·7713	1·4239	91·2
34 ..	82·2	104	0·7721	1·4245	90·6
35 ..	84·1	36	0·7586	1·4186	79·2
36 ..	85·9	10	0·7464	1·4128	73·0
37 ..	87·7	5	—	—	—
38 ..	89·5	15	0·7271	1·4041	59·0
39 ..	91·3	4	0·7174	1·4000	49·7
40 ..	93·1	55	0·7178	1·3990	59·1
41 ..	93·9	16	0·7178	1·4007	47·2
42 ..	96·7	17	0·7150	1·3997	42·5
43 ..	98·4	17	0·7180	1·4014	42·5
44 ..	100·2	82	0·7274	1·4058	76·3
45 ..	102·0	200	0·7452	1·4133	64·3
46 ..	103·8	10	—	—	—
47 ..	105·6	25	—	—	—
Residue		357			
Total ..		2072			

The distillation curve was plotted from these figures, and the amount over in each 1° C. interval read off. These figures are plotted as dm/dt in Fig. 6 against the corresponding value of t, the temperature taken as the mean of the 1° C. interval.

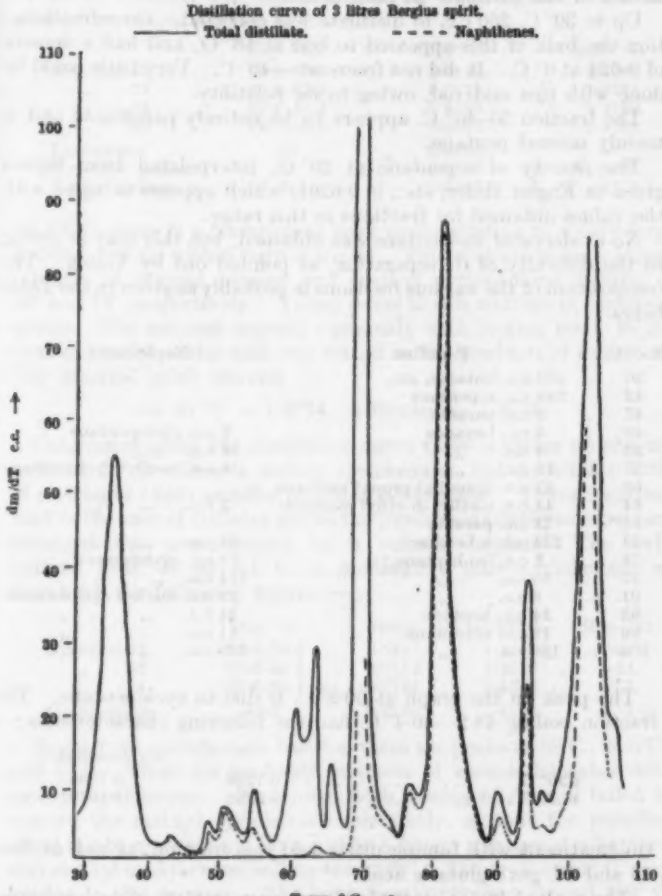


FIG. 6.

The proportion of naphthenes as calculated from the specific refractivities were also plotted, and in the same figure this curve for naphthenes is given. The interval between the two curves corresponds to paraffins. No great accuracy is claimed for the paraffin-naphthene ratio, but the curves probably give a good idea of the nature of the distillate at each point.

Up to 30° C. 250 c.c. of distillate was collected. On refractionation the bulk of this appeared to boil at 13° C., and had a density of 0·624 at 0° C. It did not freeze at —40° C. Very little could be done with this material, owing to its volatility.

The fraction 30–40° C. appears to be entirely paraffinoid and is mainly normal pentane.

The density of n-pentane at 20° C., interpolated from figures given in Engler Hofer, etc., is 0·6261, which appears to agree with the values obtained for fractions in this range.

No evidence of iso-pentane was obtained, but this may be owing to the difficulty of its separation, as pointed out by Young. The composition of the various fractions is probably as given in the Table below :—

To ° C.	Paraffins.	Naphthenes.
30 ..	250 c.c. butanes, etc.	
42 ..	244 c.c. n-pentane	
47 ..	9 c.c. paraffin	
49 ..	3 c.c. hexanes	3 c.c. cyclopentane
53 ..	4 c.c. „	16 c.c. „ „
57 ..	13 c.c. „	8 c.c. methyl cyclopentane
62 ..	53 c.c. dimethyl propyl methane	
64 ..	44 c.c. methyl di-ethyl methane	2 c.c. „ „
67 ..	23 c.c. paraffin	
74 ..	233 c.c. n-hexane	94 c.c. „ „
78 ..	5 c.c. iso-heptane ?	24 c.c. cyclohexane
87 ..	30 c.c. „	214 c.c. „ „
91 ..	9 c.c. „	12 c.c. methyl cyclohexane
93 ..	24 c.c. heptane	31 c.c. „ „
96 ..	12 c.c. n-heptane	11 c.c. „ „
106 ..	138 c.c. „	210 c.c. „ „

The peak on the graph at 50·5° C. is due to cyclopentane. The fraction boiling 48·2—50·4° C. had the following characteristics :—

		Cyclopentane.
d20° C.	0·7238 ..	0·7506
n_D20° C.	1·3988 ..	1·4079

On treatment with fuming nitric acid this fraction, as well as Nos. 15 and 16, gave glutaric acid.

The peak at 48·5° C. is probably a binary mixture of cyclopentane, with low-boiling point hexanes. The peak at 55° C. is also probably due to a binary mixture, in this case of hexanes with methyl cyclo-

pentane. Acetic acid was present in the products of treatment with fuming nitric acid.

At 61° C., 63·5° C., and 65·5° C. there are peaks which appear to be entirely paraffinoid. Young points out the presence of two hexanes (Isohexane and diethyl methyl methane) boiling near 61° C. in Galician and American spirits. The figures below are given for comparison :—

	B.p. ° C.	d20° C.	n_D20° C.
Fraction 22 ..	58·6–60·4 ..	0·6630 ..	1·3760
„ 23 ..	60·4–62·3 ..	0·6579 ..	1·3738
„ 24 ..	62·3–64·1 ..	0·6598 ..	1·3738
„ 25 ..	64·1–65·9 ..	0·6642 ..	1·3768
Iso-hexane ..	58 ..	0·6660 ..	—
2-methyl pentane	62 ..	0·6540 ..	1·3727
2-ethyl butane ..	64 ..	0·6650 ..	1·3776

At 69° C. there is a tremendous peak corresponding to a very large fraction boiling within narrow limits. This appears to be a binary mixture of normal hexane and methyl cyclopentane boiling at 69° and 72°, respectively. Young refers to this mixture in American spirits. The mixture reacted vigorously with fuming nitric in the cold and much acetic acid was traced in the products of oxidation. The residual spirit showed

$$n_D\ 20°\ C. = 1·3774 \quad \text{n-Hexane} = 1·3734.$$

Continuing along the distillation curve there is rather an obscure peak at 76° C. This is mainly cyclohexane, but contains a little of a straight chain paraffin probably iso-heptane. Young mentions that in the case of Galician petrol the purest hexamethylene fraction obtained was accompanied by a volatile heptane. The well-marked peak at 80—81° C. is moderately pure cyclohexane as shown by the following figures :—„

	B.p. ° C.	d20° C.	n_D20° C.	M.p. ° C.
Fraction 32 ..	76·8–78·6 ..	0·7617 ..	1·4187	—
„ 33 ..	78·6–80·4 ..	0·7713 ..	1·4239 ..	−11
„ 34 ..	80·4–82·2 ..	0·7721 ..	1·4245 ..	− 5
Cyclohexane ..	80·5 ..	0·7780 ..	1·4258	+ 4·5

Beyond the cyclohexane fraction there are peaks at 88 C., 92·5 C., and 94 C. These are probably mixtures of various heptanes with methyl cyclohexane. Treatment with fuming nitric acid failed to remove the methyl cyclohexane selectively, so that the paraffins could not be separated. Young gives a binary mixture of n-heptane and methyl cyclohexane boiling below 98°. The peak at 95° C. may be due to this mixture. The large fraction boiling around 100° C. is very largely naphthenic, almost certainly methyl cyclohexane, and the paraffin content is no doubt n-heptane.

The fractionation has not been carried much above this point, but an Engler distillation indicates a fair proportion of octanes.

Collecting all the figures together, the composition of the Bergius spirit as received is, approximately, as follows :—

		% wt.
	Unsaturateds	3·1
Aromatics	Benzene	2·7
	Toluene	1·9
	Xylenes, etc.	2·9
Paraffins	Butanes, iso-pentanes, etc.	10·8
	n-pentane	10·5
	Iso-hexane, etc.	6·3
	n-hexane	10·0
	Iso-heptane, etc.	2·9
	n-heptane	6·5
Naphthenes	Cyclopentane	0·8
	Methyl cyclopentane	4·5
	Cyclohexane	10·3
	Methyl cyclohexane	11·4
	Residue	15·4
		100·0

The residue contains both paraffins and naphthenes.

The authors wish to acknowledge the financial assistance received from the Distillers Company, Limited, and the Fuel Research Division of the Department of Scientific and Industrial Research towards the expenses of this research.

The Effect of Water on Aniline Points.

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven, B.Sc., F.C.S.

The aniline point of a liquid, more especially a petroleum fraction, is the cloud temperature of a mixture of it with an equal volume of aniline. From experiments with normal paraffins from pentane to nonane, Tizard and Marshall came to the conclusion that open chain paraffins all had an aniline point of 70° C., and that the presence of closed chain paraffins depressed the aniline point in the proportion of about 0·3° C. for each 1 per cent. of naphthenes present (*vide Journal*, **34**, 591, 1922).

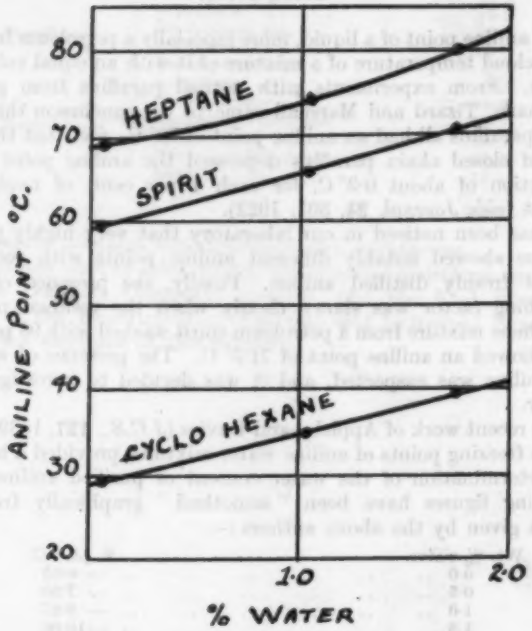
It has been noticed in our laboratory that very highly purified heptane showed notably different aniline points with successive lots of freshly distilled aniline. Finally, the presence of some disturbing factor was shown clearly when the residual paraffin-naphthene mixture from a petroleum spirit washed with 98 per cent. acid showed an aniline point of 71·5° C. The presence of water in the aniline was suspected, and it was decided to investigate the matter.

The recent work of Appleby and Davies (*J.C.S.*, **127**, 1839, 1925), on the freezing points of aniline water mixtures provided a basis for the determination of the water content of purified aniline. The following figures have been "smoothed" graphically from the figures given by the above authors:—

Wt. % water.	F. pt. ° C.
0·0	— 5·95
0·5	— 7·50
1·0	— 8·85
1·5	—10·00
2·0	—10·90

Some "pure redistilled" aniline from the chemical dealers was dried over broken caustic potash with frequent shaking to remove some 2 per cent. of water. After long standing the clear aniline was poured off through a filter into a large distilling flask. The distillation was carried out using a bare thermo-couple for the determination of distilling temperatures. In spite of the potash drying, small quantities of water appeared in the neck of the flask and were carried over into the air condenser used. After getting rid of this water as far as possible by heating the neck of the flask

and drying the condenser, the distillation was continued, the practically colourless distillate being collected in a flask fitted with a soda-lime tube. About 90 per cent. of the aniline taken was collected, distilling certainly within 0·1° C. The freezing point was —6·2° C., corresponding to 0·07 per cent. of water. Two mixtures were made up from this containing 1·02 per cent. and 1·75 per cent. of water, respectively, as determined by the freezing points. With



these three aniline water mixtures aniline points were determined on (*a*) pure heptane ; (*b*) a petrol spirit ; (*c*) cyclohexane.

The following results were obtained :—

Water content of aniline ..	0·07%	1·02%	1·75%
Heptane	68·4° C.	74·3° C.	80·0° C.
Spirit	59·4° C.	65·3° C.	70·1° C.
Cyclohexane	29·2° C.	34·5° C.	39·3° C.

In the presence of the largest amount of water the aniline point was somewhat obscure in the case of heptane and the spirit, owing

to distillation of water up the sides of the tube. The above figures are shown in the accompanying graph. The curves appear to be practically linear over small ranges of water addition, and the rise of aniline point is 6·2° C. for 1 per cent. of water in the case of heptane and the spirit and 5·6° in the case of cyclohexane. This, of course, at once suggests a method for determination of small quantities of water in spirits, etc. An aniline method has already been described in this connection by Wood and Neale (*Journal* 32, 471, 1925).

From the above figures the aniline point of pure heptane, using thoroughly dried aniline, would be 68·0° C. In order more certainly to confirm the purity of the heptane a portion of this was treated with sulphuric acid of 101·4 per cent. H_2SO_4 strength. The refractive index (n_D 20° C. 1·3875) and aniline point remained unchanged within the limits of experimental error. Apparently, therefore, where in reference to the same heptane where we have given the value 71° C. for the aniline point (*Journal* 3, 171, 1922) wet aniline was used.

Comment on Mr. W. H. Cadman's Paper, "The Origin of Hydrogen Sulphide in Persian Natural Gas."*

By Murray Stuart, D.Sc., Ph.D., F.G.S., F.C.S.

In endeavouring to establish a relationship between the occurrence of gypsum and the presence of sulphur in petroleum when the gypsum occurs in or near the oil-bearing formation, the fact should not be lost sight of that the gypsum may be a hydrochemical metamorphic product brought about by the action of meteoric water containing oxygen and carbon dioxide in solution, making its way down from the surface through formations containing both carbonate of lime and sulphide of iron. High temperature or pressure is not required to effect this reaction, which can be seen taking place to-day in the Trans-Indus Salt Range of the North-West Frontier of India. The action of such meteoric water on sulphide of iron is to oxidise it, with the result that sulphuric acid is liberated, and this sulphuric acid then reacts with carbonate of lime, giving rise to calcium sulphate. Not only is the sheet of gypsum that is forming to-day over much of the Bahadur Khel saltfield due to this reaction, but it is obvious that the massive beds of gypsum that surround the Bahadur Khel field and extend through the Salt Range had a similar origin. Both $CaCO_3$ from ordinary limestone, and $CaCO_3$ from dolomite, seem to be converted into gypsum in this way, which is fully described and illustrated in the present writer's paper on the rock salt deposits of the Punjab and Kohat, published in part 1, Vol. L, of the *Records of the Geological Survey of India* (1919).

The hillocks of gypsum (locally called "gatch") which form the most striking surface features of the oilfields at Maidan-i-Naftun carry one's mind irresistibly to the gypsum that exists on and around the Bahadur Khel saltfield, and suggest the possibility that the gypsum of the Maidan-i-Naftun oilfields may have had a similar origin.

Mr. Cadman refers to Prof. De Bröckh's personal experience that in various oilfields in the world sulphur is invariably found in considerable quantity when the oil is obtained from a dolomitised

---

* *J. Inst. Petr. Techn.*, Vol. II., No. 52, pp. 487–489, 1925.

limestone of lagoon formation, provided that gypsum also occurs in, or near, the main limestone.

Now, it is a well-known fact that as soon as a part of the sea is cut off from open circulation with the ocean and free circulation of the water ceases, such stagnant places are characterised by the development of sulphuretted hydrogen in the lower layers of the water.* Leaving out of the question the particular form in which the material now occurring as oil in dolomitised limestones of lagoon formation originally became incorporated in the limestones, it would appear therefore that it must have passed originally through water in which sulphuretted hydrogen was being generated, and it seems reasonable to expect that it would become associated with, or possibly be affected by, a certain amount of sulphuretted hydrogen. Consequently, the presence of sulphur in such oils at the present day is almost to be expected. In addition to the material which now occurs as oil being affected by sulphuretted hydrogen, which was being generated in the water through which it settled to the bottom, any ferruginous sediment that settled through the water would have a portion, if not all, of its ferruginous matter converted into sulphide of iron.

In a stagnant lagoon, such as has been postulated, if the formation of limestone was followed by a period of deposition of sediments, with occasional intervals during which thin layers of limestone were accumulated, the strata so accumulated would almost certainly contain a quantity of iron in the form of iron sulphide, and such strata when consolidated and subsequently exposed to the action of percolating meteoric water at, or near, the earth's surface would undergo hydrochemical metamorphism with the resulting formation of gypsum. The close association of gypsum with sulphur-bearing oil obtained from a dolomitised limestone of lagoon formation is to be expected therefore, but in the sequence of events outlined above the gypsum is a subsequent product in the rocks and not an original constituent of them. It is possible, of course, that a certain amount of the gypsum occurring in deposits so accumulated may be a chemical deposit that was contemporaneous with the other members of the series in which it is interbedded, particularly so when rock salt is also present, but undoubtedly most of it would appear to have been formed subsequently in the manner outlined above.

The presence of sulphur in such oils, and the existence of gypsum in close association with the dolomitised limestone of lagoon formation which contains the oil, both seem to be explicable by the fact that the materials composing the rocks, amongst which the material which now occurs as oil must be considered as an integral portion,

* *Vide* Dewhurst, *J. Inst. Petr. Techn.*, Vol. X, No. 44, p. 403, 1924.

accumulated in water in which at times, if not continuously, sulphuretted hydrogen was being generated; the sulphur in the oil and the sulphur in the gypsum being cognate. The above actions and reactions would take place at the normal temperatures and pressures obtaining at or near the earth's surface, and it seems unnecessary to assume chemical action between members of the paraffin series and calcium sulphate due to either thermal or dynamo metamorphism to account for the presence of sulphuretted hydrogen in the oil.

Reply to Discussion on "The Principles of High Vacuum Distillation of Mineral Oils."

Dr. Steinschneider wrote in reply to Mr. C. O. F. Jenkin,* as follows:—If all joints in the apparatus and in the piping of a high vacuum plant are thoroughly tight, if the plant is not excessively forced, and if the air pump—and this is extremely important—is in order, it is certainly possible to attain in the still an absolute pressure which is far lower than 75 mm. mercury column.

Instances can be cited in which the absolute pressure, measured at the air pump, is only 20 mm. mercury column, and in which this pressure is never exceeded because distilling operations are constantly under competent technical supervision.

In continuous distilling plant it is not intended that the regulation of the oil flowing through the stills shall be brought about by varying the pressure in the individual stills, but that the pressure shall be equal in all the stills, and when operations are properly conducted this can be ensured.

If the pressure in the vapour space of the still be lower than 20 mm. mercury, steam cannot be used; at such lower absolute pressure the condensation of the steam cannot be carried out practically by means of cooling water.

In the paper it was explained that, at higher absolute pressures in the vapour space of the still—of, for instance, 75 mm. mercury column—the partial tension of the oil vapours can be reduced to an absolute pressure of 20 mm. mercury column, and less, when steam is injected—that, therefore, in such case, the lowering of the boiling point can be equal to, and even greater, than when distilling under an absolute pressure of 20 mm. without using steam.

The B.K. high-vacuum plant can, moreover, work at absolute pressures which lie far below 20 mm. mercury column; then, of course, distillation must be effected without steam, and this has, as a matter of fact, already been successfully carried out.

It is well known to the author that in the United States a patent has been granted for plant for which the principal claim advanced is distillation under a pressure lower than 25 mm., and on the occasion of his recent visit to that country he closely investigated plant of this system. American patent practice admits of such patents; in European States, however, where patent applications are subjected to rigorous examination, the claims made would scarcely lead to the granting of a patent.

---

* *Soc. Inst. Petr. Techn.*, Vol. XI. 53, p. 533, 1925.

Whether any noteworthy advantage can be attained with this system in all cases is, taking into consideration the redistillation required, questionable, and in each instance special investigation is, in the author's opinion, essential. With B.K.M. high vacuum plant redistillation is unnecessary or reduced to a minimum.

STUDENTS' SECTION.

The meeting of the London Branch of the Students' Section of the Institution of Petroleum Technologists, which was held at Aldine House on December 15th, 1925, took the form of an open discussion on "Modern Production Methods." The subject was introduced by three short papers, as follows:—

Location. By E. Clark.

Production. By J. O. Tanner.

Refining. By H. S. Garlick.

The reading of the papers was followed by a discussion.

REVIEWS.

Oil-Field Exploration and Development. By A. Beeby Thompson. London: Crosby, Lockwood and Son, 1925. 2 Vols. £3 3s. per vol.

Vol. 1 (Oilfield Principles) of Mr. A. Beeby Thompson's treatise represents the results of twenty-five years' personal experience of the industry, supported by that of his able colleagues, and the compilation of much valuable information from various sources acknowledged by the author, specifically or in general.

The whole constitutes a mass of information presented in a most interesting form by one enthusiastic in his wide subject. This publication, which is perhaps the most complete of its kind in the English language, should appeal to all interested in the oil industry.

The photographic and other illustrations are good and representative of the wide scope of the volume; but the maps would have been considerably improved by the use of red or other distinctive colour for designating oilfields and oil occurrences in general, which are in many cases somewhat difficult to detect. Many instructive tables and graphs are given.

More careful proof-reading would have eliminated the somewhat frequent misspellings and misprints. For instance, the well-known name of de Golyer is misspelt in at least two different ways; while to the eminent Hungarian Professor Hugo de Böckh (Dutch nationality) is ascribed by the prefix "van" in one instance. Incidentally the Geophysical Surveys referred to on p. 421 we understand to have been carried out by Hungarians, not Austrians. Place names are in some cases misspelt; *e.g.*, Qaigarak (Mesopotamia) for Qaiyarah (spelt Quigaraly in the index); Padaukin for Padaukpin, in Burma. Some other more or less obvious misprints are Ghazif for Ghazij (p. 481); Gigensis for Gingensis; Virlete for Virleti (p. 496), etc. On page 11 is an obvious slip, where the Cambrian is referred to the "end" instead of the beginning of the Palæozoic Period. These, however, are comparatively insignificant blemishes in a work of outstanding merit.

We are glad to see the scope and the limitations of the Petroleum Geologist clearly stated at the outset.

The broad principles governing the geographical and stratigraphical distribution of oil are clearly explained, the importance of geosynclinal zones being rightly emphasised.

The respective geological age of the world's oilfields is given in Table II.; but it is to be noted that Rumania is only credited with Pliocene oil, though we have Prof. Voitesti's authority for the fact that Miocene, Oligocene and Eocene are also in some measure productive.

The Cretaceous (Nubian sandstone) source of petroleum in Egypt is also omitted. Again the age of New Zealand oil (Miocene and Cretaceous) is not stated. The comparative importance up to the present of the different series as sources of production is indicated in Table III.

The much debated question of the Origin of Oil is dealt with in the practical manner characteristic of the treatise. All unbiassed readers will surely agree that the author has effectually disposed of Inorganic Theories, as far as accumulations of economic importance are concerned. The question is discussed at length, the author, however, apparently favouring a dual origin from the "lower forms of animal life or the macerated remains of plant life."

The parts played by anærobic bacteria and salt are fully discussed.

An interesting section is given on the Relationship of Paraffinous and Asphaltic-Base Oils in which attention is drawn to the fact that, according to the author's observation, oil of the latter character is never found below Paraffinous oil in the same structural unit, though the converse is frequently the case.

It is demonstrated that there is no general relationship between density and depth.

Sulphur and its Relationship to Density of Oils forms the subject of an interesting section.

The author considers vertical migration to be confined to areas of high flexuring and faulting or of igneous intrusion. He cites the occurrence of different grades of oil at different horizons as evidence against vertical migration on many folds; while a further strong argument produced against vertical migration is the absence of purification which usually ensues when oils are forced through fine sediments.

In the chapter on Characteristics of Oil Measures it is necessary to point out that "gypsiferous shales of a petroliferous nature" in an inadequate and rather misleading description of the Lower Fars correctly described later on p. 460.

The Thermal Gradient of Oilfields is one of the subjects which receives attention, and which forms what appears to be an important line of investigation, as observations on various fields have shown that the proximity of edge-water is indicated by rise of temperature.

The great importance of geological mapping is rightly emphasised. Considering the very varied productions which are seen under the title of "Geological Map" we should have welcomed the inclusion of one or two good coloured examples (with sections) to show what should be expected to form the basis of a geologist's report on an area, where surface evidence is available. The method of portraying sub-surface structure by means of underground contours which is described, is illustrated, however, by appropriate maps.

Oilfield structures are classified, and those of many fields of different types—we might almost say, every conceivable type—illustrated either by authentic or hypothetical sections.

A long chapter is devoted to Oil Indications and their significance. With regard to Coorongite, it is to be noted that de Hautpick's theory of origin does not agree with that suggested in Redwood's Treatise.

Under Phenomena associated with the Development of Oilfields the following subjects are ably dealt with: Economic Spacing of Oil Wells, Yield and Life of Oil Wells, Production and Life of Oilfields, and Drilling Hazards.

A valuable series of chapters deals in turn with the geology of the various Oilfields—productive and merely prospective—of America, Europe, Asia, Australasia and Africa. But few countries with oil indications are omitted from these informative chapters. However, some mention might have been made of Timor, New Guinea Mandated Territory, and Afghanistan to make the list still more complete.

Certain statements regarding geological conditions in Persia in connection with the occurrence of oil are somewhat misleading.

First, the oilrock of the main producing field—the Asmari Limestone—is not Eocene as stated on p. 461, but Lower Miocene.

Nor is there authority for the suggestion that all the gas is dissolved in the oil (p. 345).

In view of the fact that the known salt domes of Persia are situated hundreds of miles from any developed oilfield they cannot be correctly referred to as "associated" therewith (see p. 197).

The initial production of wells in the Stoney Creek Field, New Brunswick, now represents a considerable increase on the figures given. In fact, we are reliably informed that recent wells have varied roughly between 30 barrels and 110 barrels initial production.

The last chapter is on the subject of "Properties and Treatment of Petroleum," which includes Physical and Chemical Properties, Uses, Distillation and Refining.

The Index appears to be complete and worthy of the treatise.

S. L. J.

REPORT OF THE SPECIAL AMERICAN PETROLEUM INSTITUTE "COMMITTEE OF ELEVEN" TO THE FEDERAL OIL CONSERVATION BOARD.

The above report, published in August, 1925, is a comprehensive estimate of the probable future supply and demand of Petroleum and its products in the United States of America. It was the Committee's intention in the first instance to forecast future demand for a period of 175 years; *i.e.*, to the year 2100, but this ambitious attempt was cut down to the more practical period of 50 years or to the year 1975.

In considering future supplies the following sources are dealt with:—

1. Production from existing wells and proved acreage by present methods.
2. Further production from existing wells and proved acreage by new and more efficient means.
3. Production from unproved acreage estimated at 1,100,000,000 acres.
4. Production from oil-shale.
5. Production from coal and lignite.

Naturally such a report, based as it is on the views of all the leading oil men in the country, has attracted widespread interest and comments. Its conclusions have been authoritatively criticised in America, and a careful study of its contents inclines one to the view that in several respects such criticism is not entirely unmerited.

The estimates of future demand being based largely on probable future increase in population, cannot call forth much criticism and form a sound basis for consideration of the future supplies required. An interesting feature, however, is the very wide difference in the figures for maximum and minimum future requirements of crude oil.

The maximum is based on present refining practice and present methods of consumption, while the minimum is based on extended use of improved cracking processes raising the average gasoline yield from the present average of 33 per cent. to 55 per cent. and a doubled efficiency of gasoline engines.

Future demand is based on the estimated requirements of gasoline and lubricating oil, fuel oil being more or less ignored as, if necessary, it can be replaced by coal.

The maximum crude demand estimated for 1975 is 1,797,439,000 bls., or roughly, 2½ times present production, while the minimum demand is only 598,538,000 bls. or 4-5ths. of the present production, so that future consumption will be largely governed by efficiency in the use of crude oil.

Turning now to the question of the oil reserves of the United States, the Committee is on more speculative ground, and one must examine the figures put forward from a more critical standpoint.

Just as the U.S. Geological Survey and other reports of 1915, 1918 and 1921 undoubtedly erred on the side of pessimism concerning future oil reserves, so the present report seems to exaggerate the extent of available reserves. Whilst it is now generally agreed that the U.S.A. reserves of free oil far exceed

the 9,150,000,000 bls. estimated in 1921, the methods used in the present report, to calculate future reserves, appear in some respects to be somewhat dangerous.

Referring specifically to proven oilfields, it is estimated that the future production of oil will be 5,300,000,000 barrels by present known methods, but it is calculated that there will then remain in the ground some 26,000,000,000 barrels of oil, a considerable portion of which can be recovered by known but partially tested methods. Assuming the proved oilfields acreage to approximate 3,200,000 acres, this represents a further quantity of, say, 8,000 barrels per acre, and a supply equal to about 42 years based on the 2,000,000 barrels per day demand of 1925. This figure of subterranean contents is probably no exaggeration, as there is now abundant evidence that in many cases not more than 20 per cent. of oil contents of the sands has been abstracted from fields approaching economic exhaustion by present methods, on the other hand, to regard this as a potential reserve needs qualification. There is now general agreement amongst oil technologists that large additional quantities of oil can be extracted from some fields which no longer yield oil through the medium of drilled wells, but it is not generally admitted that these methods are universally applicable or that they will result in a five-fold yield of oil.

Water, gas and air drives, restoration of pressure and unwatering will probably only be possible on a commercial scale in quite restricted areas, and mining methods impose such enormous expense, or are liable to be attended by so many difficulties in the majority of oilfields, that they are unlikely to assume large proportions.

There is little disposition on this side of the Atlantic to view the American statistical situation with concern, as it is felt that there are many regions which will respond to the activities of enterprising explorers and wild-catters. When, however, some 1,100,000,000 acres of country covered by sedimentary rocks are referred to as a "billion acre reserve" the authors would appear to be overstepping the mark of caution. Even assuming that America is endowed with an unusual wealth of oil, few European Geologists would be willing to admit that more than a mere fraction of this acreage would yield oil in commercial quantities.

Several statements in the report attract especial notice. Some of the most striking declarations made are that (p. 29), "most experts agree that in most oilfields intensive development with closely-spaced wells will bring forth more oil than slowly-developed fields with widely spaced wells" and (p. 54), "The sub-committees' work leads it to conclude that our present competitive drilling and producing policies result in a maximum recovery of oil by flowing and pumping methods. Competitive drilling compels the rapid completion of more wells than are compatible with maximum operating profit, but it is the general opinion of the industry that every well drilled in the field adds to the number of barrels of oil recovered by flowing and pumping," and (on p. 55), "Present production methods are as efficient as is warranted by the value of the product handled. The waste in the industry is virtually negligible, and the oil left in the ground becomes a *reserve for the future*."

These sweeping statements from such an authoritative body cause serious reflection. Whilst some of the conclusions are not entirely in conflict with observations made outside America, they do appear to need qualification. It is somewhat depressing to the economist in search of means for securing larger yields and cheaper production to be met by such views, and there are certainly many who entirely disagree with these opinions. Even if cost of production is subordinated to maximum output within a minimum of time, it is felt by many that improved ultimate yields would be obtained in many

deep fields by the better control of gas and the strategic location of wells with regard to structure. Regulated flow and rational drilling programmes on new structures would certainly reduce the "unavoidable" losses of gas, with its gasoline contents, and save enormous expenditure on competitive drilling and above ground storage for flush production which cannot be handled by available facilities. It is unusual to treat as reserves, oil left in the ground after the economic exhaustion of an oilfield by present methods, although in some isolated cases there might be ample justification for so doing.

When referring to the influence of edge and bottom waters (p. 55) the interesting view is expressed that the "bottom water is either shut off effectively or in some instances used to advantage in producing oil"; and "that edge water does not injure as much as it aids production." This view is a reversal of that generally held, but, subject to qualifications, not out of accord with the ideas of European oil technologists. It would, however, be difficult to convince Galician operators, for instance, that the water in the Tustanowice oilfield was performing a kindly action on their behalf.

The somewhat surprising statement is made on p. 23 that the physical wastage of oil between the oil well and the consumer only rarely reaches 3·3 per cent., but an analysis of the figures shows that these losses are only calculated between the *field storage* and the refiner. In the detailed figures the losses between field storage and refiner are placed at only 1·15 per cent., the balance of 2·15 being in the refineries and distribution business.

It would, therefore, appear that the main sources of loss are entirely disregarded, for it is in the production of oil that the chief waste is permitted. Considering that in 1924 De Golyer estimated that 53·2 per cent. of the U.S.A. output was obtained from 1·6 per cent. of the wells in production, it is there that the great losses of oil must be looked for, and not in the settled production areas or in transportation.

The report then proceeds to estimate the quantity of oil available from oil-shales and coal distillation. Equally optimistic figures are presented concerning the oil reserves from these sources. The known oil-shales are estimated at 394,000,000,000 short tons, from which the recovery of crude oil is placed at 108,000,000,000 bls.,or an average of only 9·6 Imperial galls. per ton. This is equal to 148 years supply at the rate of 720,000,000 bls. a year. Doubtless this quantity of oil-shales will be considerably exceeded when more geological work has been done, but to what extent these shales can be profitably worked time alone will show. Certainly we are still a very long way from being able to treat 10-gallon shale profitably.

Experience elsewhere has indicated that payable seams of workable thickness and regularity are comparatively few, and that it has never hitherto paid to mine mixed grade material. As sources of emergency oil these shales could not, at present, be relied upon to yield quantities that would seriously relieve a situation of anxiety, any more than low-temperature carbonisation of coal could be employed to alleviate the European situation during the European war. The enormous capital outlay in plant and the heavy calls upon labour for oil-shale operations must always restrict such developments. Hitherto oil-shales have only been worked at a profit when the conditions were extremely favourable as regards labour, markets and outlet for by-products, and often the nitrogen content has alone been the means of keeping the industry alive. Unless heavily subsidised or very favourably placed for cheap development and treatment it is unlikely that oil-shales will repay development for many years. The largest U.S.A. reserves of shales are situated in rather remote and difficult country in the Mid-Continental area, far removed from industrial centres and seaboard.

Especially noteworthy is the fact that coal and lignite are named as potential oil reserves. The reserves of these minerals down to a depth of 3,000 ft. are provisionally taken at 2,461,260,000,000 tons, from which a minimum oil recovery of 525,560,000,000 bls. of oil has been deduced. If coal and lignite are regarded seriously as sources of oil supply many other countries, including England, could boast of large oil reserves. At the moment, however, we prefer to seek more tangible sources.

The report concludes with a discussion on Supply and Demand for oil products, and it is admitted that in formulating productions one treads on very uncertain ground. Future oil requirements are closely connected with the relative price of coal and oil, and by developments and improvements in prime movers, Cracking Processes and gas gasoline extraction methods have entirely changed the gasoline situation within recent years, and a moderate rise in price would be followed by newer types of engines using less fuel. The coal interests, whilst at present suffering from the presence of cheap and abundant oil, will not remain idle. Suction gas plants and the use of pulverised or emulsified coal in internal-combustion engines or under boilers offer possibilities of importance, all of which have an important bearing on future oil requirements.

Admitting that the oil reserves are calculated on rather too optimistic a basis, and that some of the statements as to economic development and oilfield waste are open to question, the report undoubtedly contains an immense amount of carefully compiled statistics of the greatest value to those connected with the oil industry either in the United States or elsewhere.

A. B. T.

CURRENT PETROLEUM NOTES.

Alberta's Petroleum Situation.—Dr. John Allen, Professor of Geology at the University of Alberta, in a comprehensive survey of the Petroleum situation in Alberta, at the Annual Meeting of the Canadian Institute of Mining and Metallurgy, gave the following summary :—

In the Alberta area, 235,000 square miles, of which approximately 80,000 square miles has petroleum possibilities, wells drilled to 1925 numbered about 96, wells completed about 15, and wells being drilled in August, 1925, 15.

The oil production in Alberta from 1915 to 1924 was only 60,000 barrels, but the present production from Royalite No. 4, Turner Valley, is about 500 barrels per day, very high gravity gasoline, 73 degrees Beaumé, and the possible production from British Petroleum's Well No. 3B, Wainwright, about 100 barrels per day.

" Considering the area in Alberta with petroleum possibilities and the extremely small amount of drilling that has been carried out, there are excellent opportunities for the investment of capital in actual drilling operations in many parts of Alberta, where geological conditions are favourable for oil accumulation," said Dr. Allan, in conclusion.

World's Greatest Wet Gas Well.—According to C. O. Stilman, president of the Imperial Oil Company, the most significant event during 1925 in Canada's endeavour to make herself independent in the matter of a petroleum supply, was the spectacular development in the Turner Valley, south of Calgary. Since 1914 this field has produced high-grade crude oil in small quantities, also a considerable quantity of " wet " gas, which is stripped of its gasoline content. In an endeavour to test the deeper strata for oil in larger volume a well was carried down beyond the previously tested sands, and encountered some 18,000,000 cub. ft. per day of gas carrying crude naphtha in suspension. For the past year this well has produced 500 barrels of naphtha per day. A scrubbing plant has been installed at the well, and the gas is now being piped to Calgary for domestic purposes.